

R. J. Reid, Jr.





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A TEXT-BOOK OF
**QUANTITATIVE
CHEMICAL ANALYSIS**

BY

GRAVIMETRIC, ELECTROLYTIC, VOLUMETRIC
AND GASOMETRIC METHODS

WITH SEVENTY-FOUR LABORATORY EXERCISES

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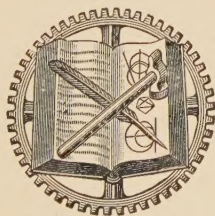
*THE ANALYSIS OF PURE SALTS, ALLOYS, MINERALS
AND TECHNICAL PRODUCTS*

BY

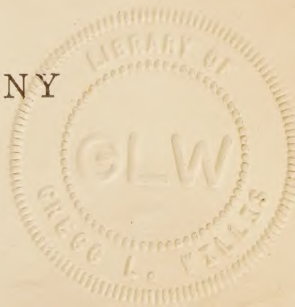
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PREFACE.

IN writing the present book the author has endeavored in the first place to produce a text-book on Quantitative Analysis which shall meet his own needs in presenting the subject to his students. The text-books available did not give as thorough and at the same time as comprehensive a view of the subject as seemed desirable. In order to present the subject from the theoretical as well as from the practical standpoint, reference by the student to a very considerable number of text-books and journals seemed necessary. This was largely due to the fact that each author has given special prominence to a particular branch of the subject, such as gravimetric, electrolytic, volumetric, or gas analysis. In the present text-book the endeavor has been made to accord each of these subjects the relative prominence which is justified by the extent to which the methods concerned are actually used. Obsolete methods and new methods which have not come into general use have generally been excluded.

In the arrangement and presentation of the subject-matter the needs of the student rather than the experienced analyst have been kept continually in view. The needs of the student have been taken to be the acquisition of a thorough comprehension of the reasons for each step in an analysis as well as the development of the skill in manipulation which is necessary in rapid and accurate work. It is believed that by this method the requirements of the professional chemist will also be best served when a reference book is needed.

The order in which the various general methods are taken up is that used by the author in instructing his classes. The instruction on the manipulation of the balance and general operations

is first given. Then the determination of metals and acids in pure salts is taken up, each student making one determination under each of the general methods given. Instruction is then given in the separation of the elements in connection with the analysis of alloys and minerals. The list of alloys and minerals whose analyses are given was selected with the object of affording practice in the separation and determination of the metals and acids which are commonly found associated together. It was thought undesirable to spend much time studying the separation of elements which rarely occur together either in nature or in the arts.

Although the chapters on Electrolytic and Volumetric Methods follow those on the analysis of minerals and alloys, electrolytic and volumetric methods have been given in these analyses for the determination of individual elements when these methods are decidedly better than the gravimetric methods. Such analyses are most advantageously made while studying electrolytic or volumetric methods.

The analyses of iron and steel, coal, water, fats, and oils are given at the end of the course to afford practice in general analytical work and also to illustrate methods of determining elements present in very small amounts.

The chapter on Stoichiometry was written to help overcome the shortcoming so often met with in otherwise excellent chemists, namely, the inability to make the necessary analytical calculations rapidly and accurately. The author realizes that only a large amount of practice will give the desired facility, and therefore would urge the student as well as the instructor to pass over no problem which is not thoroughly understood. Most of the methods of calculation have been given through the book in the exercises to which they apply.

Free use has been made of the text-books published on the various branches of analytical chemistry. The author has aimed to acknowledge in each case the source from which methods have been obtained.

The author takes great pleasure in acknowledging the obligations he is under to those who have so cheerfully assisted him in preparing this work. He is especially grateful to Dr. A. C. Lang-

muir, who has read the entire manuscript as well as proof, and who has made numerous valuable suggestions at all stages of the work. The author is also under special obligation to Mr. Albert Seeker, who read the entire proof with great care and calculated the factors given in Table II, page 470. To Professors I. W. Fay and Samuel Sheldon of the Polytechnic Institute, and to Professor Chas. M. Allen of the Pratt Institute, as well as to Messrs. Geo. C. Whipple, Lincoln Burrows, and Geo. M. S. Neustadt, the author is under obligations for suggestions and corrections on portions of the book.

The drawings for the cuts were made under the supervision of Professor Constantine Hertzberg of this Institute by Messrs. Walter Rapelje, C. A. Benoit, and Albert Seeker, to whom the author wishes to express his obligation. Several cuts were kindly loaned by Messrs. Eimer & Amend and by the Edison Manufacturing Company.

J. C. OLSEN.

POLYTECHNIC INSTITUTE OF BROOKLYN,
May, 1904.

PREFACE TO THIRD EDITION.

Two editions of this text-book having been exhausted since its publication, four years ago, the author has taken advantage of the printing of the third edition, to make such corrections and additions as his own experience and that of a number of its users, who have been kind enough to suggest improvements, has shown to be advisable. The author has endeavored in this revision to adhere to the original plan of the work, namely, to describe no method which has not been thoroughly tried in his own as well as other laboratories and found to be satisfactory, believing that only after continued use by many workers are all the conditions necessary to the successful carrying out of a method discovered, so that it can be accurately described.

The new methods which have been introduced in this edition are principally the following. Penfield's method¹ of determining water has been described because it is believed that this simple and accurate method should be more widely known. The precipitation of nitric acid by means of nitron is important as the only gravimetric method for determining this common acid. The rotation of the anode or cathode in electrolytic determinations has proved so advantageous that its use is fully described, as well as the use of electric and water motors for this purpose. The methods for analyzing water have been revised and brought into better accord with the standard methods adopted by the American Public Health Association. The simple bacteria count in water and the test for coli have also been described, as the preparation of the culture media requires considerable chemical skill. A description of various methods of determining specific gravity as well as the determination of the calorific value of fuels has also

been introduced, since chemists are so often called upon to make such determinations. A number of typical chemical problems have been introduced throughout the book in order to develop the ability to make chemical calculations, which seems so difficult for many students to acquire.

A number of less important additions have been made throughout the book, among which may be mentioned: Rules for using and cleaning platinum ware; volumetric methods for determining antimony, copper, and testing shellac for rosin. The method of determining the Polenske value, the flash point, and the viscosity of fats and oils, as well as the separation of mineral from animal and vegetable fats and oils. All atomic and molecular weights as well as the table of factors have been recalculated by the 1908 table of atomic weights. The description of methods has been improved wherever experience has shown the necessity.

While the author has given the precautions necessary to obtain correct results with all methods described, he has endeavored to avoid producing a book which can be followed mechanically with the production of good analytical results, but poor chemists. In writing the exercises he has assumed that the student has studied the text-book and knows the reason for each step in an analysis. The author is of the opinion that the student cannot successfully perform these exercises unless he has carefully studied and understood the text. It is undoubtedly for this reason that the book has not been found adapted for use in large laboratory classes where a sufficient number of competent instructors has not been provided.

The author has been very much encouraged by the favorable reception accorded the book in the past and hopes for a still larger field of usefulness in the future. He takes this opportunity of thanking all those who have been kind enough to point out errors or suggest improvements. He desires especially to express his obligation to Mr. Albert Seeker for the revision of the chapter on oils and fats and to Mr. Andrew Mayer, Jr. chemist with the National Lead Co. for the revision of the chapters on the analysis of alloys.

J. C. OLSEN.

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QUANTITATIVE ANALYSIS.

INTRODUCTION.

1. Object of Quantitative Analysis.—A quantitative analysis has for its purpose the determination of the proportion in which one or more constituents exist in a compound substance. While in a qualitative analysis the object is to prove the presence or absence of a given constituent, in the quantitative analysis the amount of the constituent must be determined. Unless the constituents of the substance examined are already known, the qualitative must precede the quantitative analysis. The student of the latter art must therefore be familiar with the former. In quantitative analysis most of the methods employed may be grouped in two classes designated as GRAVIMETRIC AND VOLUMETRIC methods.

2. Gravimetric Methods.—In a gravimetric determination the substance to be determined is separated from the other material present and weighed. It may be separated either as an element or as part of a compound which is of definite composition, and which can be obtained pure and be weighed accurately. Copper, for instance, by means of an electric current, may be deposited from a solution of a copper salt in a bright coherent form so that it may be readily washed, dried, and weighed. It may also be precipitated as sulphide, which can also be washed, dried, and weighed. As the percentage of copper in copper sulphide is known, the amount of copper present may be readily calculated.

3. Volumetric Methods.—In a volumetric determination a solution is used which contains a known amount of a substance

which can react in a definite manner with the constituent to be determined. The volume of this so-called standard solution which is just sufficient to complete the reaction is measured and the weight of the constituent to be determined is calculated. The volumetric determination of silver may be carried out as follows:

A pure chloride, such as sodium chloride, may be weighed out and dissolved in a measured amount of water. This solution is added in small quantities to the silver solution, until the metal is completely precipitated. The volume added is measured by means of appropriate instruments, and the amount of sodium chloride necessary to precipitate the silver is computed. Since one molecule of sodium chloride, or 58.5 parts, is necessary to precipitate one atom of silver, or 107.9 parts, the weight of the silver may be readily calculated.

4. Relative Advantage of the Two Methods.—Equally accurate results in general may be obtained by either gravimetric or volumetric methods, though in the case of a given substance the best method known may belong to one or the other class. Gravimetric processes and manipulations are generally simpler, while volumetric determinations usually require less time, provided the standard solutions are once prepared. Where many determinations must be made volumetric methods are preferable, while single determinations may usually be conducted more rapidly by gravimetric methods.

5. Skill and Knowledge Required.—The successful carrying out of a quantitative determination by either of these general methods requires a large amount of skill in manipulation as well as chemical knowledge. This is evident from the consideration that a correct quantitative analysis requires that both solutions and solids be carried through numerous operations without loss. The operator must also have a very complete knowledge of the chemical reactions taking place, so that he can be certain that the products finally weighed are absolutely pure and contain all of a given constituent. This is rendered the more difficult as the complexity of the substance analyzed increases. The precipitates obtained from complex substances are very apt to be contaminated with some of the elements present which alone would

not be precipitated. Only careful testing and laborious purification of such precipitates will insure correct results.

6. Patience and Honesty Necessary.—The ways in which errors may be made, especially by the inexperienced worker, are so numerous that unless the greatest care is taken in carrying out the work the results will certainly be worthless. Persons who are not conscientious enough to reject determinations in which avoidable errors are known to be present, such as spilling a part of a solution, should not undertake quantitative analysis. To the beginner the numerous precautions seem to require almost endless patience and expenditure of time. If a sufficient amount of laboratory practice is taken, the worker will ultimately acquire the skill which enables him to carry on rapidly and without error the most difficult operations. A skilful worker may also operate on many determinations at once, having learned to economize his time. A reputation for producing absolutely trustworthy results fully repays the analyst for the time and labor expended. Absolute truthfulness and patience are therefore personal qualities indispensable to the successful analyst.

7. Neatness.—In order to be absolutely certain of one's analytical results a number of habits must be acquired by rigidly adhering to fixed rules of procedure. All apparatus must be kept perfectly clean, and the working-table and surroundings in a neat and orderly condition. No assurance can be given of the accuracy of an analysis which has been carried out in vessels from which material remaining from former work may not have been removed. It does not help matters to say that one does not think there could have been enough impurity to affect the result. Absolute certainty on this point is required of the chemist.

8. Records.—One of the most common sources of error is found in the careless recording of results. Weights are frequently recorded on loose pieces of paper, backs of envelopes, etc., which may obviously be easily lost. Frequently the figures are accompanied with no indication of the nature of the substance weighed or the analysis carried out. The only safe method consists in always recording the weights or other observations in a *laboratory note-book* kept for the purpose, and keeping this original record for future reference. The page should be distinctly and fully

headed with the date, the nature of the determination, and number of the analysis or other mark of identification if several similar determinations are being carried out. The weights or other observations should be carefully verified when the record has been made. All subsequent records or observations on this determination should be made on this page. A brief outline of the method of analysis should be written on the page opposite that on which the weights and other figures are recorded. This outline should be written before the analysis is begun. The student should study the process until the reason for each step is clear. The mechanical operation of carrying out an analysis according to directions without understanding the process is of very little value.

9. Calculation of Results.—When the accuracy of the record of the work has been assured, the most common general source of error is found in the calculation of the result. Many chemists who are otherwise very capable find the calculation of their results very difficult. The student is therefore advised to pay special attention to the method of calculating the results of his determinations in the exercises given in this book as well as carefully solving the problems given for practice. Unless these rather simple calculations are thoroughly understood, he will find himself utterly unable to interpret the results in the many complicated analyses the chemist is called upon to perform. It need hardly be said that mere multiplication and division should be carried out correctly, and yet as a matter of fact many reported results are erroneous for this reason alone.

10. Limit of Accuracy.—While the analyst must be certain of the accuracy of his records and calculations, and of the cleanliness of his apparatus and surroundings, he must not make the mistake of doing part of his work with a far greater degree of accuracy than the remainder. If he weighs a precipitate to the fourth place of decimals and multiplies this weight by the percentage to which the element sought is present, the result need not be carried out to the sixth or eighth decimal place. If, for instance, a precipitate of barium sulphate weighed .4325 gram, on multiplying this number by .5886, which represents the percentage of barium in barium sulphate, the figure .25456950 is obtained. The last four figures of this number are absolutely without significance and must

be discarded. As the weight of the barium sulphate was taken to but four places after the decimal point, the amount of barium present cannot possibly be calculated to more than four places and should be given as .2545 gram. Similarly, if an analysis is carried out by a process or for a purpose in which an error of one per cent may be present, no pains need be taken to secure much greater accuracy than this in any part of the process.

That *unavoidable errors* exist in all analytical methods, no matter how carefully carried out, is beyond dispute. The experience of all workers proves that it is impossible to carry through an analysis twice, and obtain exactly identical results. With the greatest possible care, results will differ by an amount which for a given method can be made to approach a certain minimum value. For a considerable number of quantitative methods this error is .1%. Some duplicates may agree more closely than this, while others will differ somewhat more widely. The average error in a series of results will be found to be at least .1%. Most quantitative methods have a tendency to give a high or a low result because of impurities in the substance weighed or measured, or failure to obtain all of it. The quantitative result is therefore always a more or less close approximation to the truth, with a general minimum difference from the true result of .1%. Results are therefore generally computed to hundredths of per cent, though in most cases the number in the second place after the decimal point is of very little significance. It simply helps to establish the correct number in the tenths place.

There is therefore very little need of making measurements or weighings closer than 1 part in 1000. The ordinary analytical balance gives the true weight of a substance within one or two tenths of a milligram. If the amount weighed, therefore, is 200 milligrams, the error of weighing is about the same as in the remainder of the work. If a gram is weighed out, the error in weighing is 1 or 2 parts in 10,000, which is usually a much smaller amount than can be estimated in the remainder of the work. The analytical chemist, therefore, need generally spend no time or effort in overcoming an error which is less than .1% or which in the ordinary analysis amounts to less than a few tenths of a milligram. The larger the amount of the substance taken for

analysis, the more accurate will be the result if due care is taken. The time consumed in handling increasing amounts of chemicals soon becomes excessive, so that a limit of from $\frac{1}{2}$ to 1 gram in the weight of the precipitate is found advisable in practice. If a constituent is present in very small amount, a very large amount of the substance to be analyzed must be taken to obtain enough of the constituent to work with.

11. Utility and Importance of Quantitative Analysis.—The art and science of quantitative analysis is of fundamental importance to most branches of chemistry. Historically, rapid strides in the theory of the subject were made only after the necessity was recognized of taking into account the proportions in which elements combine by weight. The most fundamental conception of the atom is that of a portion of matter possessing a definite weight. The chemical formulas which are so generally used and seem to express so much are primarily expressions of the results of a quantitative analysis of the compounds concerned. In the industrial world we find one manufacturing process after another coming under the control of the analytical chemist, who tests the purity of the raw materials and the finished products and reduces the loss of valuable material to a minimum. Andrew Carnegie, the famous iron and steel master, tells us that he was the first man in America to employ a chemist for the iron and steel industry. To-day every part of the process is guided by the chemist's analysis of the material, and every plant is equipped with a chemical laboratory. Many other industries are similarly controlled by the chemist. In the commercial world an increasing number of substances are daily bought and sold on the value assigned by the chemical analysis.

In view of the fundamental importance of the subject to the science and art of chemistry and to its industrial and commercial applications, the student is urged to spare no pains to acquire the most thorough knowledge of the subject and the greatest possible skill in its application.

CHAPTER I.

THE BALANCE.

12 Construction.—The chemical balance consists essentially of three parts, namely, the *beam*, *post*, and *pans*. An agate or steel triangular prism, called a *knife-edge*, is securely fastened to the centre of the beam, and a similar one to each end. An agate or steel plane is fastened to the post, and on this plane the beam rests, the contact being formed by the central knife-edge. The pans are suspended from the ends of the beam by means of agate or steel planes set in pieces of metal called *stirrups*. These planes rest on the terminal knife-edges of the beam. The object of this method of supporting the beam and pans is to enable the system to oscillate with the least possible friction. A long, slender pointer is attached to the centre of the beam. The oscillations of the beam can be observed by means of the movements of the end of this pointer across the front of a scale attached to the bottom of the post. In this manner very slight movements may be observed. By means of a thumb-screw a second beam can be raised or lowered, so as to lift the real beam of the balance off its knife-edges when the balance is not in use, or lower it into place when it is desired to make a weighing. Adjustable supports are also provided for the pans. A levelling device is attached to the post, so that by means of thumb-screws under the balance its position may be adjusted so as to place the post in an absolutely vertical position. The instrument is enclosed in a glass case in order to protect the parts from dust and mechanical injury, as well as to prevent air-currents and sudden heating and cooling of the parts during the weighing.

13. Weighing.—The weight of a given substance is obtained by placing it on one of the pans and placing weights on the other pan until the pointer indicates the same position of the beam as

it occupied when the pans were empty. The smallest fractional* weights are obtained by moving a bent wire called a *rider* along the beam and placing it on the various divisions of the beam until an exact counterbalance is obtained. The rider must

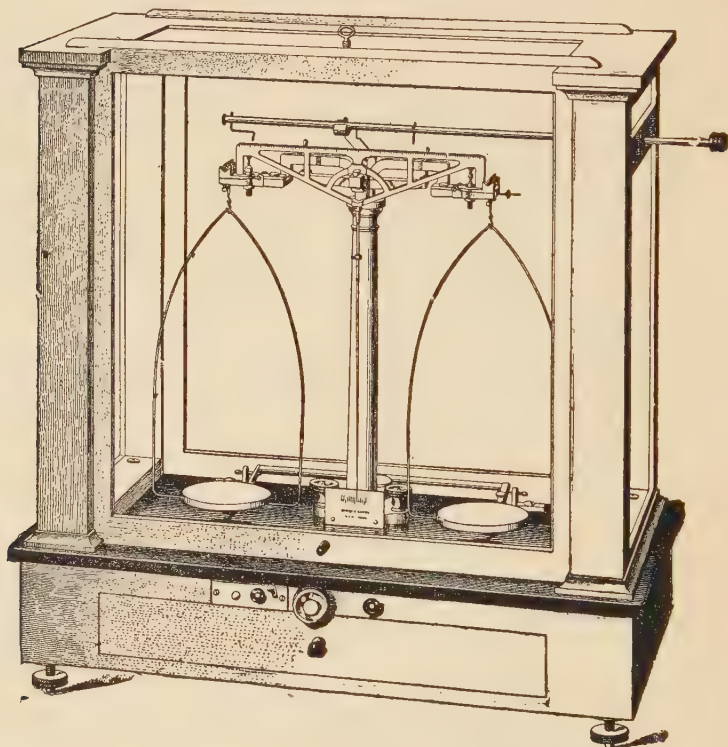


FIG. 1.

weigh as many milligrams as the total number of divisions of the beam, the last division being directly over the terminal knife-edge, and the zero-mark being directly over the central knife-edge. Balances are usually constructed for riders of 6 or 12 milligrams. As the 6 or 12 divisions of the beam are each divided into 10 parts, the smallest weight indicated by the rider will be the tenth of a milligram.

* All weights of a denomination less than one gram are called fractional weights.

It will be observed that the chemical balance gives the equality in weight between the substance to be weighed and the weights used. We assume that if the earth attracts two substances equally, they are equal in mass. *When a substance has been weighed in a balance, it can be stated that its mass is equal to the*

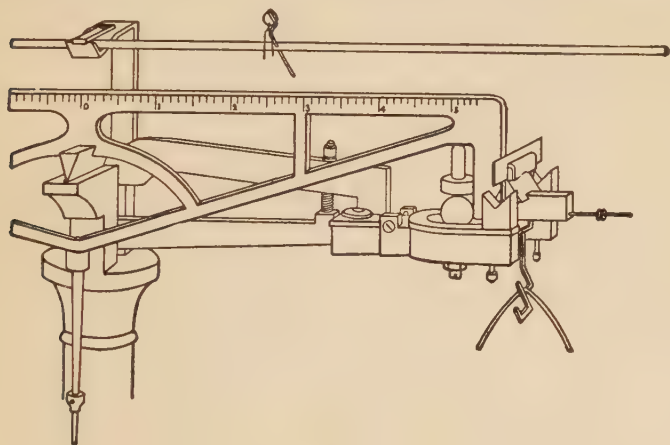


FIG. 2.

mass of the weights used to counterbalance it. If the force of the earth's attraction should vary, it would act upon the masses on the pans equally; therefore the weights found are independent of the force of gravity at the time and place of weighing.

14. Sensibility.—The beam, pans, weights, etc., constitute a system which operates in many respects like a *pendulum*, of which the central knife-edge is the point of support about which the system oscillates. The centre of gravity of the system must be below the central knife-edge, for if it were at the knife-edge the system would remain at rest wherever placed; while if it were above the knife-edge, the beam would be in unstable equilibrium. *The nearer the centre of gravity is to the central knife-edge, the more sensitive the balance becomes.* A small weight is fastened to the pointer by means of a screw. By raising this weight the centre of gravity may be brought nearer and nearer to the central knife-edge. As this is done, a smaller and smaller weight will be found necessary to displace the beam a given distance and move the

pointer through a given angle or over a given number of divisions on the scale; that is, the balance becomes more and more sensitive. By inspection of Fig. 3 it is evident that if the centre of gravity were at *A*, a displacement of the oscillating body through a given angle, *C*, would raise the centre of gravity a greater distance than if it were located at some higher point, as at *B*. The oscillations become slower and slower, however, so that a balance should not be made more sensitive than is required for the work at hand.

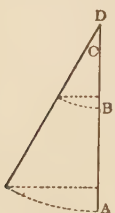


FIG. 3.

When the weights are placed on the pans of a balance, the position of the centre of gravity is not changed if the terminal knife-edges of the beam are in the same straight line with the central knife-edge, because the weights act as if placed on the terminal knife-edges. However, the rate of oscillation decreases with increasing load. If the beam bends, the terminal knife-edges are lowered, and consequently the centre of gravity of the system is lowered and the sensibility of the balance decreased. Even if the beam does not bend, the increased friction with increased load decreases the sensibility. Some balance-makers place the terminal knife-edges slightly above the one in the centre, so that when the balance is loaded the sensibility increases until the beam bends sufficiently to bring the terminal into the same plane with the central knife-edge, after which the sensibility decreases with increasing load.

The sensibility of a balance for a given load is obtained by loading the pans equally and noting the number of divisions of the scale the pointer is moved by adding a one-milligram weight to one of the pans. *Sensibility is defined therefore as the number of divisions of the scale through which the pointer is displaced by a load of one milligram.*

15. Zero-point.—When a weighing is to be made it is found more convenient and more accurate if, instead of waiting until the beam and pointer come to rest, one ascertains where they would come to rest. This is done by noting the points on the scale to which the pointer swings, and then calculating the point of rest. When the beam with empty pans is set swinging, it will seldom be found that the pointer tends to come to rest with the point at

the zero-point of the scale. An adjustable weight is attached to the end of the beam, so that by moving it from or toward the central knife-edge the pointer may come to rest very near the zero-point of the scale. In practice it will be found impossible to keep the balance adjusted so that the pointer shall indicate exactly zero. Unequal changes in temperature and other causes occasion variations in the point of rest from day to day, and also somewhat regular changes during each day. The point of rest is brought to the centre of the scale by adjusting the weight on the beam only when the pointer comes to rest more than one division from the zero-point of the scale. When a weighing is to be taken the balance is set swinging with empty pans, and the point of rest calculated from the movements of the pointer. This point of rest is called the *zero-point*. The readings are recorded in the following manner and the calculation made as indicated, the central division of the scale being designated 10:

	5.3	14.0
	5.6	13.6
	6.0	
Average	5.6	13.8
Zero-point	$= \frac{5.6 + 13.8}{2} = 9.7$	

16. Reducing Weights to Vacuo.—While the balance gives the true weight of a substance independent of variations in the force of gravity, the weight of the atmosphere introduces an error which is in some cases appreciable. A given substance weighs less in the air than in a vacuum because it displaces a volume of air equal to its own volume. The weights also are affected by the buoyant force of the air, but if the specific gravity of the weights and of the substance to be weighed is the same the two errors counterbalance each other. If the specific gravity of the weights be denoted by w , and that of the substance by w' , and the weight of the substance in grams by a , then

$\frac{a}{w}$ = number of c.c. of air displaced by the weights, and

$\frac{a}{w'}$ = number of c.c. of air displaced by the substance weighed;

therefore

$\frac{a}{w'} - \frac{a}{w}$ multiplied by the weight of a c.c. of air at the time of weighing gives the amount to be added to obtain the weight in vacuo.

17. Methods of Weighing.—The simplest method of weighing consists in adding or removing weights until the pointer does not move when the pans are released by a steady pressure on the button connected with the spring supporting the pans. This method will give the true weight within three-tenths of a milligram on a good balance. When the weight must be obtained more accurately, the balance is set swinging and the point of rest found by the method used for finding the zero-point. By adjusting the weights the point of rest may be made to coincide with the zero-point of the empty pans. When the highest possible accuracy is desired, the weights are adjusted until the point of rest nearly coincides with the zero-point of the empty pans. The point of rest is accurately found by reading the swings. The weight required to make the point of rest coincide with the zero-point is then calculated by means of the sensibility already found. If this sensibility is 2 divisions of the scale and the zero-point 10.1, while the point of rest with weights on the pan is 10.7, an additional weight of .3 milligram $\left(\frac{10.7-10.1}{2}\right)$ would be required to balance the object being weighed. This method is called *weighing by means of the sensibility*.

If the distances between the central and the terminal knife-edges are not equal, the true equality between the substances in the pans will not be obtained by the methods of weighing already given. The substance suspended from the longer arm will have the greater leverage, and must therefore be counterbalanced by a larger mass in the other pan. In practice it is found that balance-makers frequently fail to attain the ideal of a balance with arms equal within the limit of error of weighing. In ordinary work this source of error may be avoided by always placing the substance to be weighed on the same side. As the same error is in this manner introduced into the weight of the original substance and of the separated constituent, the percentage is not affected.

Even if constructed equal, unequal heating of the two sides of the balance may change the relative lengths of the arms of the beam. If the true weight of a substance is desired, it may be found by counterbalancing it exactly with sand, shot, or other convenient material and then replacing the unknown substance in the pan by weights until the counterbalance is exactly restored. This method of weighing is called the *method of substitution*.

Another method is to weigh a substance in one pan and then exchange weights and substance and weigh again. The mean of the weights obtained is taken as the weight of the substance. The true weight will be equal to the *square root* of the *product* of these two weights. As in practice these two weights are very nearly equal, their *mean* differs from the *square root* of their *product* by an amount far less than the experimental error.

Let R = length of the right arm, and

L = “ “ “ left arm;

w = true weight;

w' = apparent weight in left pan;

w'' = “ “ “ right pan.

From the principle of the lever,

$$w'L = wR \quad \text{and} \quad wL = w''R,$$

whence

$$\frac{L}{R} = \frac{w}{w'} = \frac{w''}{w}.$$

Therefore

$$w = \sqrt{w'w''}.$$

If the arms are very nearly equal, w' and w'' will have such nearly equal values that one may place $w = \frac{w' + w''}{2}$.

18. Testing Balance for Equality of Arms.—By this method a balance can be tested for equality of arms; for if they are equal, a substance should weigh the same in either pan. The relative lengths can be ascertained by weighing a ten-gram weight first on one pan and then on the other. A small weight will have to be

added or subtracted each time to produce equilibrium. Let these small weights be designated as m and n .

Let A = one of the 10-gram weights;

B = the second " weight;

A be the weight which is being weighed, and when it is placed in the right-hand pan its weight is found to be $B + m$, while when it is placed in the left-hand pan its weight is equal to $B + n$. If the weights as well as the arms of the balance are equal, m and n will each equal zero. If A and B are unequal or equal, and the arms of the balance unequal, m and n will be unequal. By the principle of the lever as above,

$$AR = L(B + m),$$

$$AL = R(B + n).$$

Solving these equations, we obtain

$$\frac{R}{L} = 1 + \frac{m - n}{2B}.$$

19. Errors in Weighing.—The weighing of large objects is attended by considerable error, because the surfaces condense air and water vapor, forming a layer whose thickness varies with the temperature and the degree of humidity of the atmosphere. This error may be avoided by using a counterpoise, which is identical in shape and size with the substance weighed. Another source of error arises from efforts which are made to clean objects very thoroughly, especially glass. For this purpose a vigorous rubbing is frequently given. This may give rise to a static electrification of the surface, which produces attraction or repulsion between the object to be weighed and neighboring bodies. Changes in weight to the extent of 6 milligrams have been produced in this manner. Under favorable conditions such a charge may remain from 20 minutes to half an hour before being dissipated. It is therefore advisable to allow glass vessels to stand in the balance-case at least 20 minutes after a thorough cleaning before weighing.

EXERCISE 1.

Determination of the Sensibility of a Balance.

Ascertain the sensibility of a balance by first finding the zero-point with empty pans. Then place a one-milligram weight on the right-hand pan or place the rider on the one-milligram division and again find the zero-point. The number of divisions on the scale between these two points is the sensibility for zero-load. In taking the zero-point the balance is brought into vibration by opening the door and directing a current of air against one of the pans by a quick downward movement of the hand. After closing the door, note the distance the pointer moves to the right and to the left across the scale. Read to one-tenth of the scale-divisions, taking two readings on one side and three on the other. If the readings are irregular, more must be taken until the difference between successive readings is approximately constant. Average the readings on each side and compute the zero-point or place where the pointer would stop. The computation is made as follows:

	7.7	13.8	
	7.9	13.6	
	8.2		
Av.	7.9	13.7	

$$\text{Zero-point} \dots \frac{7.9 + 13.7}{2} = 10.8$$

After adding a one-milligram weight to the right-hand pan the zero-point is determined again in the same manner. If, for instance, 7.9 was found as the zero-point with one milligram on the right-hand pan, then the sensibility will be $10.8 - 7.9 = 2.9$ divisions. The sensibility of the balance with loads of 5, 10, 20, 30, 40, 50, 70, and 90 grams is now obtained. For this purpose a 5-gram weight is placed in each pan and the zero-point taken. A one-milligram weight is added to the right-hand pan and the zero point again taken. The number of divisions of the scale between these two points is the sensibility of the balance with a load of five grams. If, when the weights of equal denomination are placed on the opposite pans, the swings of the pointer indicate that the zero-point is off the scale or very far from its centre, a small fractional weight of suitable size must be added to one pan so as to bring the zero-point near the centre of the scale. This is most conveniently done by placing the lighter weight on the right-hand pan and moving the rider until equality is nearly reached. The zero-point is then carefully taken and the rider moved one division further to the right or to the left and the zero-point taken again. The number of divisions between these two points gives the sensibility with the load used.

20. Maximum Load of Balance.—If the balance shows a marked decrease in sensibility at any given load, the limit of its safe use has been reached and no increase of the load should be made. A decrease of 50 per cent of the maximum sensibility indicates overloading of the balance. The sensibilities obtained together with the corresponding loads should be recorded in the laboratory note-book in tabular form for future use.

EXERCISE 2.

Determination of the Relative Length of the Arms of a Balance.

Determine the zero-point of the balance with empty pans. Having marked one of the 10-gram weights so as to distinguish it from the other, and calling this weight *A*, place it on the right-hand pan. Place the other 10-gram weight, which is designated *B*, on the left-hand pan. If the zero-point has not changed materially, locate it accurately by taking a set of readings. The weight in milligrams corresponding to a change in the position of the zero-point is found by dividing the number of divisions the zero-point has been displaced by the sensibility at the given load. For example, if the zero-point with empty pans was 11.1, and after *A* and *B* had been placed on the pans it was 7.9 and the sensibility with 10 grams load is 2.9 divisions, then $\left(\frac{11.1-7.9}{2.9}\right) = 1.1$ milligrams must be added to *B* to make it weigh as much as *A*. This small weight is *m*. Interchanging the weights and again taking the zero-point and calculating, we obtain another small weight to be added or subtracted from *B*, which is designated *n*. For example, let it be -2.1 mg. The relative length of the arm is obtained from the formula

$$\frac{R}{L} = 1 + \frac{m-n}{2B}.$$

In the illustration given,

$$\frac{R}{L} = 1 + \frac{3.2}{20000} = 1.00016.$$

In this case the right arm is longer than the left, and the true weight of a substance would be obtained by multiplying its apparent weight by the factor 1.00016.

EXERCISE 3.

Calibration of Weights.

For identification after calibration, one of the duplicate weights is in each case marked by a sharp steel point. In the case of the two 100 milligram weights, the unmarked one is recorded as 100 mg., while the marked one is indicated by $\overline{100}$ mg. If three weights of equal denomination are found in the same set, the third one is marked twice and two horizontal bars over its denomination serve to distinguish it from the remainder. If the arms of the balance have been found to be equal, the weights may be compared by the ordinary process of weighing. If, as is frequently the case, the arms are unequal, one of the methods already given for obtaining the true weight of a substance must be used. The method of substitution is very convenient for this purpose. A second set of weights is necessary in using this method. The weights of this set are placed on the left-hand pan only and are used merely as counterpoise. For comparison of the 10-milligram weights the 10-milligram counterpoise

is placed on the left-hand pan and one of the two 10-milligram weights placed on the right-hand pan and the zero-point taken. The other 10-milligram weight is then substituted for the one on the right-hand pan and the zero-point again taken. If these two zero-points are identical, the two weights are equal. If they are not identical, the number of divisions of the scale between them is divided by the sensibility. This gives the difference in weight of the weights compared, the heavier one being the one which gave the zero-point farthest to the left. This relation is recorded as in the following instance: $10 \text{ mg.} = \overline{10} \text{ mg.} + .1 \text{ mg.}$

In comparing the gram weights the differences may be greater than one milligram. The rider or other fractional weights must then be used to obtain equality between the counterpoise and the weights compared.

If the rider is 10 or 12 milligrams it is also compared with one of the 10-milligram weights. If the rider is 5 or 6 milligrams, it must be compared with the 5-milligram weight and these two compared with one of the 10-milligram weights. The following comparisons are also made:

10 mg. + $\overline{10}$ mg.	with 20 mg.
20 " + 10 mg. + $\overline{10}$ mg. + rider (or rider + 5 mg.)	" 50 "
50 " + 20 mg. + 10 mg. + $\overline{10}$ mg. + rider	" $\frac{100}{100}$ "
100 "	" $\frac{100}{100}$ "
100 " + $\overline{100}$ mg.	" 200 "
200 " + 100 mg. + $\overline{100}$ mg. + 50 mg. + 20 mg. + 10 mg. + $\overline{10}$ mg. + rider	" 500 "
500 " + 200 mg. + 100 mg. + $\overline{100}$ mg. + 50 mg. + 20 mg. + 10 mg., etc.	" 1 gram
1 gram + fractionals.	" 2 gram
2 grams.	with $\frac{2}{2}$ grams
2 " + $\frac{2}{2}$ grams + 1 gram	" 5 "
5 " + 2 grams + $\frac{2}{2}$ grams + 1 gram	" $\frac{10}{10}$ "
10 "	" $\frac{10}{10}$ "
10 " + $\overline{10}$ grams.	" 20 "
20 " + 10 grams + $\overline{10}$ grams + 5 grams + 2 grams + $\frac{2}{2}$ grams + 1 gram	" 50 "

21. Calculation of the Results of the Calibration.—The method of calculating the results is shown by the following example of the calibration of a set of weights. The following comparisons were made with the results indicated:

5 mg. = rider.	+ .1 mg.
10 " = 5 mg. + rider.	— .1 "
10 " = $\overline{10}$ mg.	— .1 "
20 " = 10 mg. + $\overline{10}$ mg.	+ .1 "
50 " = 20 mg. + 10 mg. + $\overline{10}$ mg. + 5 mg. + rider.	+ .1 "
100 " = 50 mg. + 20 mg. + 10 mg. + $\overline{10}$ mg. + 5 mg. + rider.	+ .1 "

100 mg.	= $\overline{100}$ mg.		-.1 mg.
200 "	= 100 mg. + $\overline{100}$ mg.		+.2 "
500 "	= fractional weights.		+.2 "
1 gram	= fractional weights.		-.2 "
2 grams	= fractional weights + 1 gram.		+.2 "
2 "	= $\overline{2}$ grams.		
5 "	= 2 grams + $\overline{2}$ grams + 1 gram.		+.5 "
10 "	= 5 grams + 2 grams + $\overline{2}$ grams + 1 gram.		+1.0 "
10 "	= $\overline{10}$ grams.		
20 "	= 10 grams + $\overline{10}$ grams.		+.4 "
50 "	= 20 grams + 10 grams + $\overline{10}$ grams + 5 grams + $\overline{2}$ grams		
	+ $\overline{2}$ grams + 1 gram.		+2.0 "

Using the 5-milligram weight as the basis of comparison and assuming for this comparison that it weighs exactly 5 milligrams, we would obtain the following values for the fractional weights, where the values to the left of the equality sign merely designate the weights being calibrated, while the figures to the right give the comparative values of these weights in terms of the 5-milligram weight:

5 mg.	= .005 gram	50 mg.	= .0491 gram
Rider	= .0049 "	100 "	= .0982 "
$\overline{10}$ mg.	= .0098 "	100 "	= .0982 "
10 "	= .0097 "	200 "	= .1963 "
20 "	= .0196 "	500 "	= .4910 "
Sum of fractional weights = .9818 "			

The one-gram weight is taken as the standard for the entire set of weights and is assumed to be correct or equal to 1.0000 gram. As the sum of the fractional weights have been found to be .0002 gram heavier than the 1-gram weight, the sum of these weights should be 1.0002 grams. As by assuming the 5-mg. weight to be correct, we obtained a total of .9818 gram, we must increase the values assigned by .0184 gram (1.0002 - .9818 gram). Half of this increase must be added to the 500-mg. weight, one-fifth to the value given to the 200-mg. weight, etc. The following values will result from this calculation:

500 mg.	= .5002 gram		(.4910 + .0092)
200 "	= .2000 "		(.1963 + .0037)
100 "	= .1000 "		(.0982 + .0018)
$\overline{100}$ "	= .1000 "		(.0982 + .0018)
50 "	= .0500 "		(.0491 + .0009)
20 "	= .0200 "		(.0196 + .0004)
10 "	= .0099 "		(.0097 + .0002)
$\overline{10}$ "	= .0100 "		(.0098 + .0002)
5 "	= .0051 "		(.0050 + .0001)
Rider	= .0050 "		(.0049 + .0001)

Assuming the 1-gram weight to be correct, the following values are obtained for the larger weights:

1 gram	= 1.0000 gram	10 grams	= 10.0031 grams
2 grams	= 2.0004 grams	10 "	= 10.0031 "
2 "	= 2.0004 "	20 "	= 20.0066 "
5 "	= 5.0013 "	50 "	= 50.0169 "

When careful work is being done the weight of a substance is obtained by using the values found by the calibration instead of those marked on the weights.

22. Weighing Substances Containing Water.—Most substances submitted to analysis may be weighed on watch-glasses without any appreciable change in weight during weighing due to loss or gain of water. If any doubt exists on this point, the substance after being exactly counterbalanced may be left on the scale-pan for about the same length of time as was required for weighing and its weight again taken. If any change has occurred, the substance must be weighed in a *weighing-bottle*. These bottles are made of thin glass with ground-glass stoppers, and may be obtained of any suitable size. The substance to be analyzed is quickly transferred to the bottle after having been brought to the condition, so far as moisture is concerned, in which it is desired to analyze it. The bottle is then weighed and a sufficient quantity of the contents carefully tipped out into a beaker or other vessel in which to operate on the compound. The stopper is quickly replaced and the bottle weighed. The difference is the amount taken out for analysis.

23. Use of Desiccator.—After a substance has been heated, and while it is cooling, preparatory to being weighed, it should be placed in a desiccator, which is a glass vessel containing a dehydrating agent, such as concentrated sulphuric acid or fused calcium chloride. A cover is ground to fit the desiccator, and the joint is made air-tight by greasing the ground surface with vaseline. In the dry air of the desiccator most substances cool without absorbing moisture. It is best to weigh a substance as soon as cool, usually in ten to twenty minutes. Some substances begin to absorb moisture as soon as placed on the scale-pan. Such substances should be weighed as quickly as possible, reheated, cooled, and weighed. In taking the second weight, however,

the weights should be placed on the scale-pan before the substance to be weighed is taken out of the desiccator, so that as soon as it is placed on the scale-pan the weight may be ascertained by taking the swings of the pointer or by moving the rider.

24. Rules to be Observed in Using the Balance.—The pans should be brushed off with a camel's-hair brush before weighing.

Care should be taken not to spill any substance whatever on the floor of the balance-case. It should always be kept clean.

Students should not adjust or attempt to repair a balance. Report any irregularities to the instructor.

All volatile liquids and acids must be weighed in closed weighing-bottles.

Only metals, alloys, and pieces of minerals should be placed directly on the pans of the balance. All other substances should be weighed on watch-crystals or in a weighing-bottle. The beam and pans must always be supported when substances which weigh more than a gram are taken off or placed on the pans.

The substance to be weighed must always be placed on the left-hand pan, and the weights on the right-hand pan.

Always count the weights twice—first, by noting the ones missing from the box; second, by noting the weights when taking them off the pan. An error in noting the weight of the substance to be analyzed frequently involves serious loss of time.

Crucibles and substances which are to be weighed must be allowed to become perfectly cold before being placed on the scale-pan. A warm substance produces a current of air which by its buoyant effect apparently lessens the weight. The amount of air and moisture condensed on the surface is always less in the case of a warm body. Allow at least fifteen minutes for a platinum crucible and precipitate to cool in a desiccator, while twenty minutes should be allowed for the cooling of a porcelain crucible under the same conditions.

Lower the support of the beam to start the balance swinging with a slow even motion so as not to damage the delicate knife-edges by suddenly bringing them against the planes. When through weighing, be sure not to leave the balance swinging, and remove the rider from the beam. Note all weights in a book. Do not use scraps of paper.

CHAPTER II.

GENERAL OPERATIONS.

A NUMBER of the operations of gravimetric analysis are common to most determinations, no matter what element is concerned or employed. The element to be determined must first be PRECIPITATED by the addition of the reagent necessary to form an insoluble compound. The precipitate must be separated from the solution by FILTRATION and WASHING, and finally the precipitate must be DRIED and WEIGHED.

25. Precipitation.—A careful study of the solubility of the various compounds of an element must be made before the most suitable form for precipitation can be selected. The most *insoluble* precipitate is generally the best form. The solubility in both hot and cold water as well as in a solution of the salts present under the conditions of precipitation must be studied. In many cases the solubility of a precipitate is very much reduced by the presence of an excess of the precipitating reagent in the solution. This follows from the *law of ionization* of a saturated solution. All inorganic salts, acids, and bases dissociate in water solution into parts called *ions*, which in the case of salts are, on the one hand, the atoms of the metal, and on the other hand the acid radical. Barium sulphate, for instance, breaks up into **Ba** and **SO₄**. Acids dissociate, giving the acid hydrogen atom **H** as one ion, and the remainder of the acid as the other ion. Bases dissociate, giving **OH** as one ion and the metallic atom as the other ion. If *a* and *b* represent the number of ions in unit volume of a solution to be precipitated, and *ab* the number of undissociated molecules, then the equation $\frac{a \times b}{ab} = c$, where *c* is a constant, expresses the relation between these quantities. Taking barium sulphate as an example, in a saturated solution of this salt there will be present some undissociated molecules, some **Ba** ions and some **SO₄**,

ions. If, now, some barium chloride molecules are added to the solution, this salt will dissociate into **Ba** and **Cl** ions. The relation of the number of ions and molecules expressed by the equation $\frac{a \times b}{ab} = c$ no longer holds for the solution, since a or the number of barium ions has been increased by the barium ions produced by the dissociation of the barium chloride. As c is found by experiment to remain constant, a change in the values of b and ab must take place. If some of the sulphate ions (b) unite with an equal number of barium ions (a), there will be produced some molecules of barium sulphate (ab), the numerator of the fraction will have been decreased, and the denominator increased. This process will continue until the former value of c will have been reached and equilibrium restored. As the solution was already saturated with barium sulphate, the added number of molecules of this salt must be precipitated. If, therefore, the salt used in precipitation is quite insoluble, an *excess* of the reagent containing one of the ions of this salt will diminish the solubility to a negligible quantity, by increasing the values of a or b in the general equation, $\frac{a \times b}{ab} = c$.

In some cases an excess of the reagent used in precipitation is to be avoided, because the precipitate *redissolves* in the excess of the reagent. Aluminium hydroxide, for instance, redissolves to an appreciable extent in an excess of ammonia, the aluminium probably acting as an acid, and forming an aluminate with the base. Silver chloride dissolves in an excess of sodium chloride or hydrochloric acid, forming a double chloride. In such cases as these, care must be taken to add only a very slight excess.

26. Contamination of the Precipitate with Soluble Salts.—Another difficulty met with in precipitation is the tendency of many salts to carry down other salts which are themselves very soluble. It is frequently impossible to wash such a precipitate free from the contamination. In many cases the precipitate must be *redissolved* and *reprecipitated*. As the solution containing the bulk of the soluble salt is separated from the insoluble salt by the first precipitation, during the second precipitation only a small amount of the soluble salt is present, and the rather small fraction of this amount which is carried down may be neglected.

Various theories have been given to account for this phenomenon. If the precipitant is added rapidly, particles of the solid will, no doubt, surround and enclose portions of the solution. For this reason it is advisable to add the precipitating reagent in a fine stream, with vigorous stirring of the solution. Heating the solution also increases the solubility of the soluble salts.

Besides the mechanical action of a precipitate, it is also undoubtedly true that more or less insoluble chemical compounds are formed by the union of soluble and insoluble salts. Barium sulphate has been shown to unite with ferric sulphate, forming a double sulphate of barium and iron which loses SO_3 on ignition, leaving the sulphate of barium colored red with ferric oxide.

27. Digestion of Precipitates.—Many very insoluble precipitates, such as barium sulphate and calcium oxalate, come down in such a fine state of subdivision, that in attempting to filter them, they pass through the pores of the paper. Such precipitates should be allowed to stand for a considerable time in contact with the mother-liquor, as the size of the particles will then increase. The same object is more quickly accomplished if the solution is boiling during the addition of the precipitant, and is then allowed to *digest* at a temperature near the boiling-point. This change in the size of the particles is due to the well-known fact that the solubility of a finely divided substance is greater than that of large particles of the same substance. If both large and small particles are present in contact with the solution, the smaller ones will tend to dissolve and produce a solution which is supersaturated with respect to the large particles. This process is quite rapid in the case of moderately soluble salts, but with the insoluble compounds used in quantitative analysis, the action is very slow. Heating the solution increases the solubility,* and therefore accelerates the solution of the fine powder. The final result of the process is that the small particles dissolve and the large particles grow in size by the addition of the small ones.

As the solubility of the small crystals is greater than that of the large ones, complete precipitation is not obtained unless the

* Though this is generally true, there are a few substances which are more soluble in cold than in hot water. Among these are lithium and strontium sulphates and calcium hydroxide.

precipitate is allowed to stand for some time in contact with the solution. Digesting the precipitate hot hastens this process, as it removes the small crystals. Shaking the precipitate thoroughly accomplishes the same object, as it hastens the solution of the small particles by bringing them into contact with the solvent and prevents supersaturation by bringing the large particles into contact with the solution.

28. Filtration.—The separation of the precipitate from the solution is accomplished by filtration. The difficulties encountered at this point are of two kinds: Finely divided precipitates pass through the pores of the paper or other filtering medium, while gelatinous solids prevent the solution from passing through. The former difficulty is overcome by digesting the precipitate with the solution in a warm place. The filter-paper should first be moistened with water, and if the precipitate comes through, the first portions of the turbid filtrate should be repeatedly passed through the filter-paper until it becomes clear. The pores of the paper will then be filled with the precipitate. The filtration is most rapidly accomplished if the solution is hot, boiling water passing through the pores of paper about six times as fast as cold water. If the precipitate is gelatinous, so that filtration is slow and the precipitate does not pass through, recourse may be had to filtration by suction. The most convenient way of producing a vacuum is by the Bunsen filter-pump. A great many forms of such pumps are on the market, varying in efficiency and durability. The paper must be fitted perfectly to the funnel, and the point supported by means of a perforated platinum cone or a small square of linen or some similar device. The piece of linen, which should be about 3 cm. square, is neatly and evenly folded on the centre of the filter-paper, which is then folded again in the usual manner. The paper must be carefully fitted to the funnel, and pressed firmly down into the apex and then held there by the index finger of the left hand while it is moistened with a little distilled water from the wash-bottle. All parts of the paper must be in contact with the glass. If the sides of the funnel are uneven, this is impossible and another funnel must be selected. A funnel whose sides curve down to the stem must always be rejected.

Very few funnels are made with the correct angle, so that the

filter-paper must generally be folded with the edges uneven, as shown at *c* in Fig. 4. If the paper as folded does not fit the funnel, it must be folded again, allowing a larger or smaller lap. When the paper has been placed in the funnel, the latter should be inserted into the rubber stopper of the filter-flask, and after filling with water the suction applied. If the paper does not break while the water is being sucked through, it has been properly fitted to the funnel and the solution to be filtered may be poured on it.

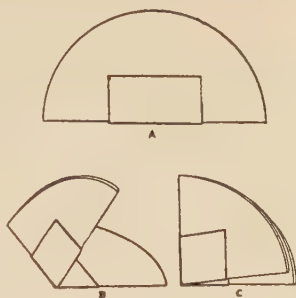


FIG. 4.

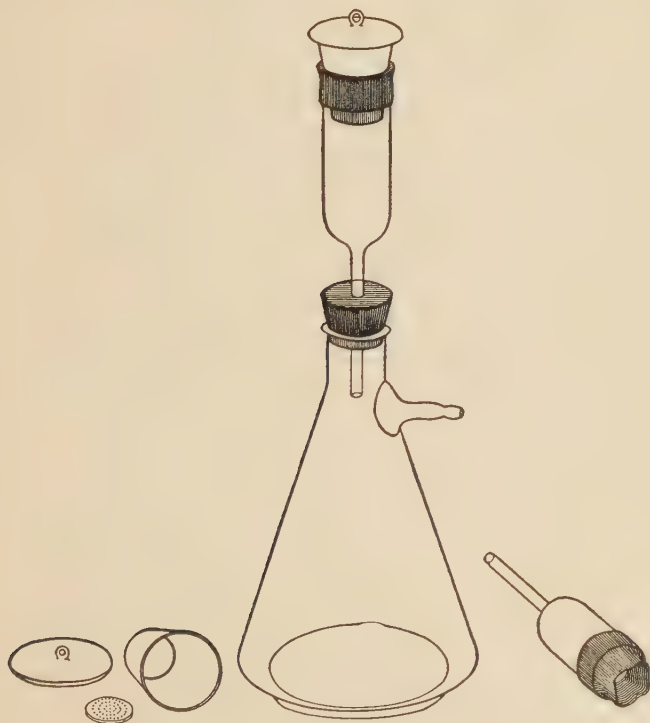


FIG. 5.

A much simpler method of filtering by suction is by the use of the GOOCH CRUCIBLE, as shown in Fig. 5. The bottom of this crucible consists of a plate which is perforated with a large num-

ber of small holes. A layer of asbestos in water is floated over the bottom and sucked down to a compact mass, the thickness of which is varied according to the fineness of the precipitate. The crucible is then connected, by means of a rubber band, with a funnel which is connected as usual with the filter-flask. Solutions which attack paper may be filtered in this manner. The Gooch crucible is especially well adapted for precipitates which must be dried at temperatures below ignition.

The asbestos must be purified by digestion with strong *aqua regia* for several hours and washing with water until free from chlorides. The asbestos is then washed into a glass-stoppered stock bottle. After the layer of asbestos has been formed in the crucible, it must be washed with water until fine particles of asbestos are no longer washed out.

29. Washing Precipitates.—When a filtering medium has been secured by means of which the precipitate can be rapidly and completely separated from the solution, the next object of the analyst is to secure thorough washing of the precipitate. Water is the most common reagent used for this purpose, and when possible, it should be hot. In some cases precipitates are insoluble in water only when other salts are present. Volatile salts, such as ammonium chloride, are used for this purpose, as the subsequent ignition expels them. When non-volatile salts must be used, they must finally be washed out with the least amount of pure water. In some cases alcohol or ammonia serves as the washing liquid. The most rapid and thorough way of washing is to leave the precipitate in the beaker and simply decant the wash-water through the paper. The precipitate may then be thoroughly mixed with the successive portions of wash-water and finally transferred to the paper and the washing completed. This process is called washing by *decantation*. When the precipitate is immediately transferred to the funnel the amount of wash-water used is less, but the time required is generally greater and the washing is less thorough. Stirring up the precipitate for this reason with the stream of water from the wash-bottle is advantageous and should be done whenever possible, and more especially when the precipitate is large. To avoid spattering, the stream of water is first directed against a portion of the paper not covered with the precipitate. In all cases the filtrate must

be tested for the constituent to be washed out, and for the final test several cubic centimeters should be taken.

The filtration and washing of gelatinous precipitates is very much facilitated by adding the paper pulp from 2 or 3 quantitative filter-papers before precipitation. As the precipitate is intimately mixed with the paper pulp the wash-water comes into intimate contact with the precipitate. On igniting such a precipitate it is left in a finely powdered state and its re-solution is comparatively easy. The filter-paper may be pulped by moistening with a little concentrated hydrochloric acid.

30. Preparation of Pure Salts.—Before applying a method of analysis to an unknown substance it is necessary to analyze some substance of known composition in order to test the method and the individual's skill in using it. Owing to personal peculiarities, individual chemists sometimes utterly fail to get satisfactory results by using methods which in the hands of others give uniformly satisfactory results. If, therefore, a method is first applied to material of known composition, the chance of failure on an unknown substance is avoided. For this purpose, pure recrystallized and carefully dried salts are most frequently used. The method of preparing a number of these salts will therefore be given.

31. Recrystallization is the method most commonly used for purification. By this process the impurities are gotten rid of in one of two ways. If insoluble, they are filtered off; if soluble, they remain in the solution when the salt which composes the bulk of the substance crystallizes out. Recrystallization also serves the important purpose of securing a product containing the theoretical amount of water of crystallization, since even a salt which is correctly called *chemically pure*, inasmuch as it contains no foreign material, may contain *varying amounts of water*.

In most cases the so-called commercial salts, instead of the more expensive chemically pure quality, may be used in the preparation of the pure recrystallized salt. If the salt is in large crystals, it should be coarsely powdered in a porcelain mortar. It is then dissolved in hot water, so as to obtain a nearly saturated solution. Any insoluble material must be filtered off. During this process, the salt will crystallize out in the filter-paper unless the funnel is kept warm. This is best accomplished by

means of some form of the *hot-water funnel*, which is a hollow metallic funnel which can be filled with water and heat applied from a Bunsen burner, as shown in Fig. 6. A folded filter-paper should be employed. If in spite of the hot-water funnel the salt crystallizes out on the paper, the solution must be diluted. The filtered solution must be stirred vigorously while the salt is crystallizing out. This prevents the formation of large crystals or aggregations of small crystals, which are very apt to enclose portions of the mother-liquor in the interstices. As soon as the solution is cold the crystals should be filtered off and as much of the mother-liquor as possible sucked out, while with a porcelain spatula or spoon the same object is accomplished by pressing the crystals into a compact mass. The remainder of the mother-liquor may be washed out by ice-cold distilled water, unless the

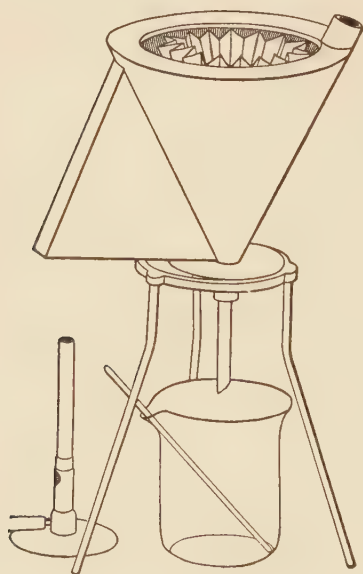


FIG. 6.

salt is very soluble. The salt should be redissolved in distilled water and recrystallized. Its purity is increased by each recrystallization, but ordinarily two crystallizations are sufficient; and if a C. P. salt is used in the first instance one crystallization is frequently sufficient.

After being freed from the mother-liquor by suction, pressing, and washing, the salt is removed from the funnel and spread out on large sheets of absorbent or filter-paper, or, still better, on a porous unglazed porcelain plate. The crystals are pressed between the paper or rubbed on the plate with a porce-

lain spatula until no more liquor is absorbed. It is then allowed to stand in the air with occasional stirring to break up large lumps and to expose moist crystals to the air until it is dry, which can be determined by ascertaining if the crystals adhere to a clean and dry glass or porcelain surface. This test must be made from time to time so that the salt shall not be exposed

for too long a time to the air, as in that case water of crystallization may be lost. When dry, the crystals must be transferred to a clean dry glass-stoppered bottle.

32. Preparation of Double Salts.—The process of recrystallization will by no means secure in the case of every salt a degree of purity sufficient to permit its use as a standard. Many salts are not easily obtained of constant composition so far as the percentage of acid and base are concerned, while others cannot be dried so as to retain a definite percentage of water. Many salts which alone cannot be prepared pure can be purified by the formation of *double salts*, especially of ammonium. The alums belong to this class as well as many double sulphates which are not alums, such as the double ammonium sulphates of zinc, nickel, cobalt, ferrous iron, as well as the double chlorides of copper, platinum, etc. Some of these double salts are so stable that they are not decomposed by solution in water, so that they can be recrystallized in the same manner as the simple salts. The alums can be purified in this manner. The less stable double salts decompose in water solution, so that part of the less soluble constituent crystallizes out first, then crystals of the double salt appear. The double sulphate of magnesium and potassium behaves in this manner. This difficulty may be overcome by having an excess of the more soluble constituent present. For this purpose and in the preparation of any of the double salts, the constituents of the double salt may be dissolved separately in hot distilled water and then the solutions mixed and vigorously stirred while the salt crystallizes out. Ordinarily the single salts may be taken in the proportion of their molecular weights. Ferrous ammonium sulphate $[\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}]$ may be made by dissolving the constituents separately in the proportions 278 to 132 [$\text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 278$ and $(\text{NH}_4)_2\text{SO}_4 = 132$] and then pouring the solutions together. As the iron oxidizes easily, the temperature of the water must not be allowed to exceed 40° , and the process must be carried out rapidly. If an unstable double salt, like potassium magnesium sulphate $(\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O})$, must be prepared, the magnesium sulphate must be present in excess to the extent of $\frac{1}{4}$ to $\frac{1}{3}$ of its molecular weight. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ having a molecular weight of 246, we must use $(246 + 80)$ 326 parts of this salt to 174 parts of the potassium sulphate ($\text{K}_2\text{SO}_4 = 174$).

33. Precipitation by Change of Solvent.—For various reasons recrystallization is not always applicable, and recourse to other means must be made. Common salt or sodium chloride differs so little in its solubility in hot and cold water that it cannot conveniently be recrystallized. Advantage is here taken of the fact that this salt is much less soluble in concentrated hydrochloric acid than in water. This property is based on the fact already explained on p. 21, that an increase in the number of one of the ions of a salt diminishes the solubility of that salt. As chlorine is one of the ions of sodium chloride and also of hydrochloric acid, the addition of the latter to a concentrated solution of the former precipitates it in large quantities. As the impurities are present in only very small quantities, the solution is very far from being saturated for these salts, even when they are chlorides of other metals than sodium. In order not to dilute the solution the hydrochloric acid is conducted into it in the gaseous form.

Sodium carbonate may be purified in a similar manner by conducting carbon dioxide into a saturated solution of the sodium salt. In this case, however, the precipitate is the more insoluble sodium bicarbonate which is reconverted into the carbonate by gentle heat. Another illustration of this method of purification is found in the preparation of pure ferrous sulphate. Recrystallization is inadvisable in this case, because ferrous salts oxidize very rapidly when their solutions are heated in contact with the air. A cold saturated solution of this salt is made and crystallized out by the addition of an equal volume of alcohol. As ferrous sulphate is quite insoluble in 50% alcohol, a good crop of crystals is obtained by stirring this mixture. The crystals are washed with alcohol and dried in the usual manner. As the moist crystals oxidize quite readily, the presence of alcohol is here advantageous, since it facilitates drying by its volatility and by displacing the water.

34. Precipitation by Double Decomposition.—*Insoluble* salts must be prepared by precipitation under conditions in which no other substance comes down. The carbonates of the alkaline earths are prepared in this manner. The chlorides and nitrates of these metals can be easily obtained in the necessary state of purity. If other metals are present besides the alkali metals, they may be removed from the solution of the alkaline-earth

COMPOUNDS OF THE METALS AND ACIDS WHICH CAN BE PREPARED IN A PURE CONDITION.

METALS.	COMPOUNDS.	Method of Purification.	Parts of the Salt Dissolved by 100 Parts of Water at				
			0°		20°		100°
Aluminium.	$\text{Al}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$	R.	3.9		15.0		357.5
Ammonium.	NH_4Cl	R.	29.7		37.2		77.3
	$(\text{NH}_4)_2\text{SO}_4$	R.	70.6		75.4		103.3
Antimony...	$\text{KSbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$...	R.		5.26 ^{7°}	7.75		35.7
Arsenic.....	As_2O_3	S.	3.7				11.5
Barium.....	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	R.	36.2		41.8		68.8
Bismuth.....	Bi_2O_3	I.					
Cadmium....	CdI_2	R.	86		92.6		133.3
Calcium.....	CaCO_3	P.					
	Iceland spar.....						
Chromium...	$\text{K}_2\text{Cr}_2\text{O}_7$	R.	5		13.1		102
Cobalt.....	$\text{CoSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$...	R.	25.4		52.4	108.1 ^{49°}	
Copper.....	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	R.	24.2		36.5		204.5
	Metal.....						
Iron.....	$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	R.	18		29.8	78.2 ^{75°}	
	Metal.....						
Lead.....	$\text{Pb}(\text{NO}_3)_2$	R.	36.5		52.3		127
Magnesium...	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	R.	76.9		119.7		671.2
	$\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$...	R.	20.3		37.2	104.6 ^{75°}	
Manganese...	$\text{MnSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	R.			51.3 ^{25°}		
Mercury.....	HgCl_2	R.	5.73		7.39		53.96
	Metal.....	D.					
Nickel.....	$\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	R.		3.5° 2.5	8.1	39.5 ^{85°}	
Potassium...	KNO_3	R.	13.3		31.2		247
	KCl	R.	28.5		34.7		56.6
Silver.....	AgNO_3	R.	122		227		940
	Metal.....						
Sodium.....	NaCl	P.	35.7		36.0		39.8
Strontium...	SrCO_3	P.					
Tin.....	$\text{SnCl}_4 \cdot 2\text{NH}_4\text{Cl}$	R.		14.5° 33			
Zinc.....	$\text{ZnSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	R.	10		17.3	67.8 ^{80°}	

In the column headed "Method of Purification," the letters have the following signification: R., recrystallization; D., distillation; S., sublimation; I., ignition of nitrate, and P., precipitation.

COMPOUNDS OF THE METALS AND ACIDS—(Continued).

ACIDS.	COMPOUNDS.	Method of Purification.	Parts of the Salt Dissolved by 100 Parts of Water at			
			0°	15°	20°	100°
Hydriodic. . .	I.	S.				
	KI.	R.	127.9		144.2	209
Hydrobromic	KH(IO ₃) ₂	R.		15° 1.53	17° 5.4	
	KBr.	R.	53.3		64.5	102
Hydrochloric.	NaCl.	P.	35.7		36.0	39.8
Nitric.	HNO ₃					
	KNO ₃	R.	13.3		31.2	247
Oxalic.	H ₂ C ₂ O ₄ .2H ₂ O.	R.			11.1	350
	(NH ₄) ₂ C ₂ O ₄	R.	2.2	15° 4.2		
Phosphoric. .	KH ₃ (C ₂ O ₄) ₂ .2H ₂ O	R.				
	Na ₂ HPO ₄ .12H ₂ O.	R.	6.3		23.4	236.8
	NaNH ₂ HPO ₄ .4H ₂ O.	R.			16	100
	KH ₂ PO ₄	R.				
Sulphuric. . .	H ₂ SO ₄					
	K ₂ SO ₄	R.	8.5		10.9	26.2

In the column headed "Method of Purification," the letters have the following signification: R., recrystallization; D., distillation; S., sublimation; I., ignition of nitrate, and P., precipitation.

metal by passing hydrogen sulphide through the acid solution, filtering off any precipitate, and then adding ammonia and again filtering. To the solution thus purified, ammonium carbonate solution is added with vigorous stirring. The precipitated carbonate is then thoroughly washed and dried. This method cannot be used for the preparation of the pure carbonates of the other metals, because these elements do not form stable carbonates of definite composition.

NOTES.

Ammonium Chloride as purchased varies greatly in purity. Phosphoric arsenic, sulphuric, and sulphocyanic acids may be present as well as heavy metals and earths and aniline derivatives. The pure salt is best prepared by neutralizing C.P. hydrochloric acid by a stream of ammonia-gas produced by heating pure concentrated ammonium hydrate. When the acid is neutralized the solution is made slightly acid with hydrochloric acid and evaporated to dryness in a porcelain dish and dried on the water-bath.

Ammonium Oxalate is examined in the same manner as oxalic acid. It does not lose water of crystallization as readily as the acid.

Ammonium Sulphate may be made by the method given for ammonium chloride, but must be dried at 120° and the solution must be neutral or alkaline before evaporating to dryness.

Arsenious Oxide may be tested for sulphide by heating 1 gram in a test-tube. The first sublimate which forms must be pure white. At the end of the operation no residue must remain in the tube.

Barium Carbonate must be prepared by precipitation of the C.P. chloride with ammonia and ammonium carbonate. The washed precipitate is gently ignited in a platinum dish.

Barium Chloride may be tested for metals by passing hydrogen sulphide through the acid solution and then rendering it alkaline with ammonia. Five grams of the salt are dissolved in 200 c.c. of water, acidified with a drop or two of dilute hydrochloric acid, heated to boiling, and the barium precipitated with sulphuric acid. After digesting for some time, the precipitate is filtered off and the filtrate evaporated to dryness in a platinum dish. The alkalies, lime, etc., will be found in the residue, which should be less than .1% in the C.P. salt.

Bismuth Oxide may be prepared pure by dissolving the commercial article in nitric acid, diluting largely with water, filtering and washing the precipitate, which may be dried and ignited in a platinum dish. A still purer product may be obtained by dissolving the basic nitrate in pure nitric acid, precipitating with ammonia and ammonium carbonate, washing and igniting.

Cadmium Iodide may be tested for tin, lead, copper, zinc, and other metals by dissolving 2 grams in water and adding nitric acid. A white precipitate indicates tin. To one-half of the solution a large excess of ammonia is added. The solution must remain clear and colorless. The other part of the solution is diluted with water and filtered after adding excess of potash solution. Pass hydrogen sulphide through the filtrate and acidify. No precipitate must be produced either in the alkaline or acid solution.

Calcium and Strontium Carbonates are prepared by the method given for barium carbonate. During the drying, especially of the calcium carbonate, the platinum dish must not be allowed to become even faintly red. It is advisable to support the dish about an inch above a wire gauze, which is heated by the Bunsen burner. A very pure form of calcium carbonate may be purchased in the form of Iceland spar.

Copper prepared electrolytically and of a high percentage of purity may be readily obtained.

Copper Sulphate.—This salt must almost invariably be recrystallized and carefully dried in order to insure the presence of the theoretical amount of water. The dry crystals on exposure to the air effloresce. The loss of water is indicated by the appearance of white spots in place of the clear blue of the hydrated salt.

Ferrous Ammonium Sulphate, frequently called **MOHR'S SALT**, may be purchased remarkably pure. The crystals should be small and free from

ferric iron. A gram of the salt dissolved in boiled water which has been allowed to cool out of contact with the air must show only a faint red with thiocyanate.

Hydrochloric, Sulphuric, and Nitric Acids may be easily obtained almost absolutely free from impurities. The percentage of acid present may be ascertained from the tables pp. 479-486 after carefully taking the specific gravity.

Iodine must always be purified by sublimation. For this purpose the commercial article is mixed with one-fourth or one-fifth of its weight of potassium iodide by grinding them together in a porcelain mortar. The material is placed in a watch-crystal or crystallizing-dish, which is placed on a piece of asbestos board having a hole cut in the centre. The iodine is sublimed by gentle heat from a Bunsen burner, the first portion of the vapor being allowed to escape as the material is frequently quite moist. Another watch-crystal or crystallizing-dish is now placed over the first one, the upper one being kept cold by means of moist filter-paper or cloth. The upper dish is removed before all of the iodine is sublimed. It is best to sublime the iodine immediately before use as it is very hygroscopic.

Iron.—The soft iron wire, which is sold for standardizing purposes, contains from .2 to .4% of carbon. For careful work the percentage of iron or carbon must be determined gravimetrically.

The DOUBLE AMMONIUM SALTS of MANGANESE, COBALT, NICKEL, and ZINC must be prepared by the general methods given.

Mercury.—On being shaken in a clean dry bottle the surface must remain perfectly bright and the metal must not adhere to the surface of the glass.

Mercuric Chloride may be tested for mercurous chloride by treating a gram of the finely ground sample with 15 c.c. of pure ether. It must dissolve completely. The filtrate from the hydrogen-sulphide precipitate must leave no weighable residue. On testing this precipitate with dilute ammonia, filtering and acidifying the filtrate with hydrochloric acid, no yellow precipitate or color must be produced indicating absence of arsenic

Oxalic Acid must leave no residue on ignition. An alkaline residue indicates the presence of sodium or potassium. Sulphuric acid is tested for by dissolving 5 grams in 100 c.c. of water, adding a few drops of dilute hydrochloric acid and barium chloride. No precipitate must form after standing several hours in a hot place. Ammonia and ammonium sulphide must produce no coloration. On heating 2 grams in a test-tube with caustic-soda solution no ammonia must be given off. A very pure acid may be made by dissolving the impure material in a mixture of equal parts of alcohol and ether, filtering, evaporating off the alcohol and ether after the addition of water, and recrystallizing the product.

Potash Alum.—Recrystallization and carefully drying may be necessary to insure the correct percentage of water.

Potassium-acid Iodate may be purchased remarkably pure. Meineke found two samples 100.001 and 100.010% pure.

Potassium Bromide and Iodide can usually be obtained quite pure. The presence of bromates or iodates is shown by the blue color produced by added starch solution and a little dilute hydrochloric acid to the dilute solution and in the case of the bromide a little potassium iodide. The heavy metals and sulphuric acid are tested for in the usual manner. The salts must be dried at 100°.

Potassium Dichromate is generally obtained very pure. The commercial samples frequently contain sulphates or chlorides. The C.P. or recrystallized salt may be dried by heating until the salt is fused. It should not be heated higher, and all organic matter must be carefully excluded.

Potassium Nitrate is also sold in a very pure condition. Manufacturers generally guarantee a maximum impurity of sodium chloride of about 1 part in 10,000 or .01%.

Potassium Permanganate, which is very nearly 100% pure, may be readily obtained. Chlorides, sulphates, and nitrates, which are present in the commercial article, are absent from the C.P. salt. The latter, however, invariably contains small quantities of manganese dioxide.

Potassium Sulphate must give a clear neutral solution (1 to 20) and must give no reaction with hydrogen-sulphide water, ammonium oxalate, potassium carbonate, or silver nitrate. It may be dried at 100°.

Potassium Tetroxalate may be prepared by making a hot saturated solution of oxalic acid, neutralizing one-fourth of it with pure potassium carbonate and adding this with stirring to the remainder of the solution. The product is still further purified by recrystallization.

Silver Nitrate.—Good commercial samples have been found to contain from .01 to .03% of impurity. The crystals should be pure white.

Metallic Silver may be obtained of a high state of purity guaranteed by government assay.

Sodium Phosphate and Sodium-ammonium Phosphate must be neutral to phenolphthalein and free from sulphates, chlorides, and nitrates. If the crystals are not transparent, but show signs of efflorescence, the salt must be recrystallized and carefully dried.

Sodium and Potassium Chlorides may be purchased pure enough for most quantitative work. The method of purification of sodium chloride given in Experiment 6 yields a very pure product.

Zinc and Magnesium Sulphates must always be recrystallized and carefully dried. The double sulphate of magnesium and potassium is prepared as directed in Exercise V.

Many of the tests given in this section have been quoted from "Testing of Chemical Reagents," by Dr. C. Krauch. The student is referred to this book or to "Chemical Reagents, their Purity and Tests," by E. Merck, for the testing of other salts.

EXERCISE 4.

Preparation of Pure Copper Sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

Weigh out about 150 grams of crystallized copper sulphate. Crush the large crystals in a porcelain mortar. Dissolve in about 150 c.c. of hot distilled water. If the solution is not perfectly clear, filter, using a folded filter-paper and a hot-water funnel. The clear filtrate must be vigorously stirred as soon as crystals begin to separate. Cool the solution by placing the beaker in cold tap-water or in ice-water. Continue the stirring until no more crystals separate out. Filter off the crystals immediately, using a funnel of suitable size with a platinum cone or a perforated porcelain dish in the bottom of the funnel. Connect the funnel by means of a rubber stopper to a filter-flask and remove as much of the mother-liquor as possible by means of strong suction from the filter-pump. Press the crystals into a compact mass by means of a spatula. Pour about 50 c.c. of ice-water over the crystals and suck it through as rapidly as possible with the suction. When no more liquid comes through, spread out the crystals by means of a spatula on an unglazed porcelain plate or on several folds of filter-paper. When no more liquid seems to be absorbed, spread the crystals out in an even layer. Cover them with a piece of filter-paper and allow them to dry in the air for several hours with occasional stirring. Test for moisture from time to time by placing a few crystals on a clean and dry porcelain or glass surface. Dry crystals will not adhere to such a surface. As soon as dry, transfer to a clean dry bottle with ground-glass stopper. Care must be taken in removing from the filter-paper not to detach shreds of filter-paper with the crystals. If the crystals have been exposed too long to the air, portions will appear white from loss of water of crystallization. If the work has been carried on in a room containing hydrogen sulphide or ammonium sulphide in the atmosphere, black spots will appear on the crystals. If such crystals cannot be removed the work must be repeated.

EXERCISE 5.

Preparation of Potassium-magnesium Sulphate, $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$.

Weigh out about 163 grams of magnesium sulphate and dissolve in 115 c.c. of water. Dissolve 87 grams of potassium sulphate in 350 c.c. of water. If necessary, filter the solutions separately, using the hot-water funnel and folded filter-papers. Pour the hot solution of potassium sulphate rapidly and with vigorous stirring into the hot magnesium solution. Stir constantly while the double salt crystallizes out, and finally cool the solution by surrounding the beaker with cracked ice. When no more salt crystallizes out, filter the crystals off in a funnel with a platinum cone or perforated porcelain plate in the bottom. Suck the mother-liquor off by means of the filter-pump, pressing the crystals together with a porcelain spatula. Wash the crystals with 50 c.c. of ice-cold distilled water, sucking them dry with the

pump. Transfer the crystals to an unglazed porcelain plate or several folds of filter-paper. Remove the mother-liquor by pressing the crystals on the porcelain plate with a porcelain spatula or by pressing them with the hand between the folds of the filter-paper. Finally, spread them out to dry in the air, testing them for moisture from time to time by placing them on a clean and dry porcelain or glass surface. The dry crystals will not adhere to such a surface. When dry, transfer to a clean and dry bottle.

EXERCISE 6.

Preparation of Pure Sodium Chloride.

About 70 grams of common salt are weighed out and dissolved in 200 c.c. of distilled water. If necessary, the solution is filtered. Gaseous hydrochloric acid is now passed into the solution. It is generated in the flask *A*, which

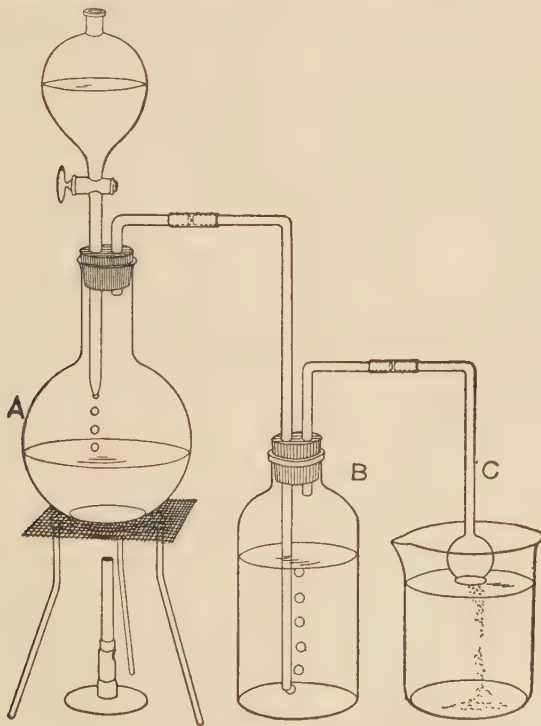


FIG. 7.

contains about 150 grams of common salt. 300 grams of concentrated sulphuric acid are poured into 220 c.c. of distilled water and allowed to cool somewhat. This acid is transferred to the dropping-funnel and allowed to drop slowly on the salt. *B* is a wash-bottle containing concentrated hydrochloric acid to catch any sodium sulphate which might spatter over. The

thistle-tube *C* touches the salt solution in the beaker. Toward the end of the operation the flask may be heated so as to expel the hydrochloric acid. The stream of hydrochloric acid is allowed to pass until no more precipitation is noticed in the salt solution. The crystals are filtered off and washed with concentrated c.p. hydrochloric acid. When no more liquid can be sucked out by the pump, the sodium chloride is transferred to a porcelain dish and heated with the Bunsen burner until dry and free from hydrochloric acid. The pure salt is then transferred to a clean and dry glass-stoppered bottle.

RULES FOR USING AND CLEANING PLATINUM UTENSILS.

Platinum when hot easily forms alloys with other metals. For this reason metals must never be heated in platinum. The same rule applies to all compounds of easily reducible metals, such as silver, copper, lead, and bismuth. Even stannic oxide is sometimes reduced to metallic tin, which alloys with the platinum.

Heat platinum only with a clear blue flame. A deposit of carbon is injurious. The vessel should also be placed beyond the inner cone of the flame, as reducing gases may pass through the hot platinum.

As phosphorus and sulphur combine with platinum, making it brittle, compounds of these elements should not be heated in platinum under reducing conditions.

Caustic alkalies should not be fused in platinum as it is oxidized and dissolved. Nickel, iron, silver, or copper dishes may be used for this purpose.

The carbonates of the alkalies may be fused in platinum, although a little platinum is dissolved, especially when potassium nitrate is present.

Platinum vessels may be cleaned by digestion with hydrochloric or nitric acids, but not with a mixture of these acids. Basic impurities not removed in this manner may be dissolved by fused acid potassium sulphate, while acid impurities such as silica may be removed by fused sodium carbonate. The surface of platinum should be kept smooth and bright by polishing with sea sand which is free from sharp particles.

Platinum vessels change weight very slowly, losing a few tenths of a milligram after strong ignition, a little more after a fusion, especially with an alkaline oxidizing mixture, and still more on being polished.

CHAPTER III.

DETERMINATION OF WATER.

35. Conditions in which Water is Held.—Water is present in the great majority of substances submitted to chemical analysis, and the amount present must frequently be determined. It may be held MECHANICALLY or combined CHEMICALLY as water of crystallization, or it may be an inherent part of the molecule. In considering its determination, the manner of separating it from the other constituents present must be studied as well as the method of weighing it. The simplest method of determining it involves heating the compound to the temperature at which the water volatilizes. This temperature differs greatly, ranging from the ordinary temperature of the air to that of the blast-lamp. Where the water is held mechanically, as in most minerals, as well as metals and non-crystalline substances, a temperature of 100° or a few degrees above that point is sufficient to dry the substance completely. In the case of salts which crystallize with water, the temperature at which it is completely given off varies from 100° centigrade to a red heat. In some cases a definite number of molecules of water of crystallization will be driven off at one temperature, while a higher temperature is required to completely dehydrate the substance. The *silicates*, as a class, hold water with great persistence. Glass may be heated to a red heat for months, and still give off a trace of water. In this case the water is probably combined with the silica, forming a more or less complicated silicic acid.

36. Methods of Determining Water.—Whenever a substance can be dried completely by simply heating it to a temperature at which no other constituent is volatilized, the amount of water may be determined by weighing the substance before and after drying it. In this case the amount of water present may also

be determined by allowing the water to be absorbed by a weighed amount of some hygroscopic substance, like calcium chloride or concentrated sulphuric acid. Such a determination would give the *total amount of water* present. This water may be present either as HYGROSCOPIC water or as water of CRYSTALLIZATION or of CONSTITUTION.

If it is necessary to determine the amount of each, the substance must first be heated to a temperature at which only the hygroscopic water is given off. At a temperature of 105° the hygroscopic water will certainly be expelled in every case, but as at that temperature many crystals lose a part or all of their water of crystallization, a lower temperature must sometimes be used. In such cases, the substance is placed in a desiccator in which the air is dried by sulphuric acid or calcium chloride. Even under these circumstances many crystals lose water. By diluting the sulphuric acid, however, an atmosphere may be obtained having a tension of water vapor equal to or greater than that produced by the water of crystallization. Long standing in such an atmosphere will free the crystal of adherent or hygroscopic water.

37. Sources of Error.—When substances lose other constituents than water on heating, the error may frequently be avoided by adding an anhydrous substance which is capable of retaining the volatile substance. The oxides of calcium, lead, and bismuth have been used as *retainers* for fluorine, chlorine, sulphur, etc.

Not only must loss of volatile constituents on heating be guarded against, but a possible increase in weight from the absorption of oxygen, carbon dioxide or air must be kept in mind. Metals in their lower state of oxidation may absorb oxygen, and pass to the higher state of oxidation. A familiar example of this is ferrous sulphate, which will absorb oxygen even at the ordinary temperature. Sulphides of some metals easily take up oxygen, becoming sulphates. Some basic oxides of the metals absorb carbon dioxide, forming carbonates. Some minerals, such as the zeolites, have been found to absorb air after the water has been expelled.

EXERCISE 7.

Determination of Water of Crystallization in Copper Sulphate,
 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

38. **Weighing the Salt.**—A watch crystal of convenient size is weighed, a one-gram weight is added to the right-hand pan and recrystallized copper sulphate is placed on the watch-crystal by means of a spatula until equilibrium is restored. Exactly one gram of copper sulphate will then have been weighed out. In placing the salt on the watch-crystal by means of the spatula, the latter should not be allowed to touch the watch-crystal nor the scale-pan. The spatula with a moderate amount of the salt in it is held in the right hand so that by tapping it gently with the left hand the crystals will fall on the watch-glass. The arms supporting the beam are slightly lowered by the central thumb-screw, so that, by releasing by means of the left hand the spring supporting the scale-pans, the pointer will indicate when enough salt has been added by remaining at zero or moving to the right. After a little experience the quickness with which the pointer moves will indicate the amount of salt to be added or taken away. When the pointer moves slowly to the left, only a few small crystals at a time are allowed to fall on the watch-crystal until the pointer ceases to move. The swings may then be taken if necessary and the final adjustment made. If too much has been added, a considerable amount should be very carefully taken off, and added in small amounts as before. *When exactly a gram is weighed out, the calculation of percentage is very simple, as the number of milligrams of water lost is equal to the tenths of per cent.* At first it may seem easier to calculate from an amount weighed out which is only approximately one gram than to endeavor to obtain exactly one gram, but it is found that an experienced worker can weigh more readily than make the required calculations.

39. **Determination of Four Molecules of Water.**—The watch-glass with copper sulphate is now transferred to an air-oven, heated to 115° . The temperature is regulated by adjusting the flame of the Bunsen burner from time to time until the thermometer indicates a constant temperature. After about one hour the copper sulphate is transferred to a desiccator, and after ten minutes weighed. It is again heated in the air-bath one-half hour and cooled and weighed. This is repeated until the weight is constant. In most analytical work a weight is considered *constant* if the change is not greater than 0.3 of a milligram, since errors of weighing may be as great as this. Frequently a change of weight of 1 milligram warrants a discontinuation of the heating, since the next heating would probably produce a much smaller change in weight. As the watch-crystal may have lost weight on heating, the copper sulphate is brushed off and the watch-crystal weighed. The difference between this weight and the last weight of the dried copper sulphate and the watch-crystal gives the weight

of the dried copper sulphate. The difference between the weight of the dried copper sulphate and of the crystals taken is the weight of water expelled. The percentage of water lost in this manner will be found to be very nearly that calculated for 4 molecules of water or 28.85%. The correct weight of the watch-crystal may also be obtained by drying it in the air-bath at 115° until its weight is constant before placing the copper sulphate on it.

39a. Determination of the Fifth Molecule of Water.—If the air-bath can be heated to 210° – 215° , the fifth molecule of water may be determined in the same manner as the first four. For this purpose either another gram of the crystals may be weighed out and the total amount of water determined or the portion from which the 4 molecules have been expelled may be heated to constant weight at 210° to 215° and the percentage corresponding to the fifth molecule determined. If the air-bath cannot be heated to 215° , the watch-crystal containing the copper sulphate may be placed on a sand-bath which consists of an iron plate filled with sand and placed on a tripod so as to be heated by means of a Bunsen burner. Until the bulk of the water has been expelled, the thermometer-bulb should be immersed in the sand so as to touch the watch-crystal, which should be

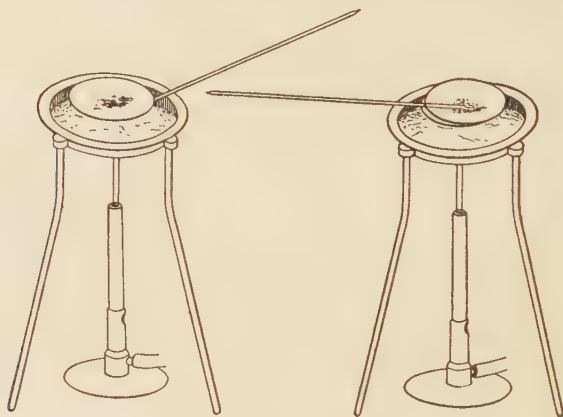


FIG. 8.

pressed down firmly in the sand. When the copper sulphate has been heated about one hour in this manner, the bulb of the thermometer, after being freed from sand, should be placed on the copper sulphate in a slanting position. The watch-crystal should be covered with another and the Bunsen burner regulated until the thermometer indicates 210° to 215° and the heating continued for one-half hour, when the copper sulphate is carefully brushed off the thermometer and the former cooled in the desiccator and weighed. The heating with the thermometer on the copper sulphate is repeated until the weight is constant. The watch-crystal is now weighed

after removing the copper sulphate and the percentage of water calculated. The theoretical percentage for 5 molecules is 36.07.

EXERCISE 8.

Determination of Water of Crystallization in Barium Chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$.

A crucible, preferably of platinum, with its lid, is placed on a pipe-stem triangle and heated with the Bunsen burner for a few minutes, cooled in a desiccator, and weighed. Two grams of pure crystallized barium chloride are weighed out and transferred to the crucible. The crucible is placed on the pipe-stem triangle and heated gently by a small Bunsen burner flame, the lid being on the crucible. The temperature is gradually raised until the crucible attains a low red heat, at which it is maintained for about ten minutes. It is then cooled in a desiccator and weighed. The heating and weighing is repeated until the weight is constant. Theoretical percentage of water of crystallization in crystallized barium chloride is 14.74.

40. Penfield's Method of Determining Water.—A very simple and accurate method of determining water, especially when it is present in small amount, is that of Penfield.* The apparatus used consists simply of a glass tube closed at one end and having one or two bulbs blown on the middle of the tube. If a high temperature is required to expel the water, a hard glass tube must be used, otherwise ordinary soft glass tubing may be used. Tubes 20 cm. long and 6 mm. internal diameter will be found a convenient size. When the amount of water given off is large, a bulb should be blown on the middle of the tube. The tube is first dried by placing in an air-bath heated to a little above 100° and sucking out the moist air by means of a smaller tube. The tube is then cooled and weighed and the substance to be analyzed is carefully transferred to the bulb at the closed end of the tube, which is again weighed, the difference between this weight and the weight of the empty tube giving the weight of the substance analyzed.

A short piece of glass tubing drawn out to a capillary is attached to the Penfield tube by means of a short piece of rubber tubing. This simple device prevents the loss of water by circulating air currents. Moist filter-paper or cloth is wrapped around the bulb in the middle of the tube, and the bulb at the end containing the

* Am. Jour. Sci., 3d series, Vol. XLVIII, p. 31. 1894.

substance being analyzed is heated high enough to expel the moisture. This may generally be accomplished with the Bunsen burner, although some substances require the blast-lamp. The water condenses on the cold middle portion of the tube and collects in the bulb, which prevents it from running back to the heated portion and cracking the glass. When all of the water has been expelled the flame is moved so as to melt off the bulb containing the substance being analyzed; when this has been accomplished the tube is cooled and weighed after removing the capillary tube at the end. The tube is now placed in the air-bath and dried as in the beginning of the experiment. It is then cooled and again weighed, the loss of weight being equal to the amount of water obtained.

If other volatile substances besides water are given off, a retainer must be used. The oxides of calcium, lead, or bismuth have been used for this purpose. The retainer need not be weighed, but it must be thoroughly dried before being placed in the tube, and enough should be added after the weighed substance to be analyzed has been introduced to fill the bulb and form a layer about two centimeters deep. The retainer must be heated first and then the flame is increased so as to also heat the bulb. When all of the water has been expelled the part of the tube containing the retainer is melted off and the determination completed as already described, when no retainer is required.

The Penfield method is well adapted to the determination of water in minerals and substances which require high heat in order to expel the moisture. The results are accurate if the operation is carefully carried out, although only moderate amounts of water can be weighed in this manner.

41. Efficiency of Various Drying-agents for Gases.—When the water is to be weighed directly, it must be absorbed in a weighed amount of some dehydrating agent. The substances commonly used for this purpose are PHOSPHORUS PENTOXIDE, CONCENTRATED SULPHURIC ACID, and FUSED CALCIUM CHLORIDE. Phosphorus pentoxide is the most efficient drying-agent for gases known. It is doubtful if any water at all remains in a gas which has been dried over this reagent. On the contrary, gases dried over concentrated sulphuric acid give up moisture to phosphorus

pentoxide, while gases dried with fused calcium chloride give up moisture both to concentrated sulphuric acid and to phosphorus pentoxide. One litre of air dried with calcium chloride at 15° C. gives up 1 milligram of water to concentrated sulphuric acid, while phosphorus pentoxide is capable of absorbing .002 milligram of water per litre after the air has been dried over concentrated sulphuric acid.

Equally correct results, however, may be obtained by the use of the less efficient dehydrating agents if care is taken to dry the air when it enters the apparatus to the same extent as when it leaves. This object is best secured by using the same dehydrating agent for both purposes. Some moisture will be present in the air which passes over the hydrated substance, but as exactly the same amount of water is present in the air on leaving the second set of drying-tubes the water actually absorbed by these tubes will be that taken up within the apparatus only.

42. Drying Properties of Fused Calcium Chloride.—When calcium chloride is used care must be taken to keep all of the tubes in a series of the *same temperature*, as this salt differs in its efficiency at different temperatures. At 0° centigrade, 1 litre of air after being dried over calcium chloride contains .3 milligram of water; if dried at 15° it contains 1 milligram of water, while if dried at 30°, 3.3 milligrams of water remain. In one experiment where air was passed through a series of U-tubes (A, B, C, D, E) filled with calcium chloride, which were maintained at different temperatures, the gains and losses in the weights noted below were observed. Before entering the first tube, A, the air was dried by passing through a tube of calcium chloride maintained at the temperature of A.

Tubes.	Temperatures.	Changes in Weight.
A.	16.9°	.0000 gram
B.	0.0°	.0452 "
C.	30.2°	.1565 "
D.	0.0°	.1569 "
E.	16.9°	.0442 "
Total change in weight		.0014 gram

It is extremely difficult to obtain fused calcium chloride which is entirely free from calcium oxide. It will, therefore, be found to absorb a small amount of carbon dioxide. To neutralize the

calcium oxide the calcium chloride should be kept in an atmosphere of carbon dioxide or hydrochloric acid for some time and then the acid gas displaced by air. This is best accomplished by filling tubes with it and passing a slow stream of the acid gas through them, and finally drawing air through. When moist air passes over calcium chloride some of it dissolves in the water absorbed, and this liquid mass on the surface of the lumps afterward solidifies. The so-called *Marshand* tube is, therefore, best adapted for use with calcium chloride. This U-tube has a bulb blown in the exit tube on one side. The moist air should be led in at this point, so that the water may condense in the bulb, which may be kept cold by moist filter-paper wrapped around it. The calcium chloride in the half of the tube nearest the bulb should be in large lumps, so that the tube shall not be clogged by the dissolved calcium chloride. The other half of the U-tube should be filled with finer material, so as to dry the gas thoroughly. A plug of glass wool should be inserted above the fine calcium chloride, so as to prevent small particles from being carried out by the current of air.

43. Drying Properties of Concentrated Sulphuric Acid.—Concentrated sulphuric acid is about equally efficient at 0° and 30° centigrade. It should be free from sulphur dioxide. If present, this gas may be expelled by passing a current of air through the acid. If the acid is at all dark or brown in color from the presence of organic matter it should not be used, as sulphur dioxide will result from the slow oxidation of the organic material. It absorbs carbon dioxide to an appreciable extent, but this is wholly expelled by passing air through it. U-tubes should first be partly filled with glass beads and then sulphuric acid added until the beads are thoroughly moistened and the liquid just forms a seal at the bottom of the tube. Care must be taken that sulphuric-acid U-tubes are always held upright, so that the acid shall not come in contact with the stoppers or enter the exit tubes. It is therefore most convenient to attach a platinum wire, so that they may be suspended during the weighing and at other times. This wire should be left on the tube.

44. Drying Properties of Phosphorus Pentoxide.—Phosphorus pentoxide is seldom used, because of the difficulty of manipu-

lating tubes containing it. When moist air comes in contact with it, a very viscous liquid is produced which very quickly prevents the further passage of gases through it. U-tubes are therefore filled with alternate layers of glass wool and the drying material. The phosphorus pentoxide must not contain any of the trioxide. If the latter is present, the material must be distilled in a stream of oxygen.

45. Making Impervious Connections.—Either cork or rubber stoppers may be used in closing U-tubes after being filled, unless they are provided with glass stoppers. Both cork and rubber are by no means impervious to moisture and carbon dioxide. The exposed surface must therefore be coated with sealing wax, paraffine, or shellac varnish. If the latter is used, a sufficient time should be allowed for the escape of the alcohol before weighing the tube.

When the tubes are connected, short pieces of rubber tubing should be used, but the glass parts of the apparatus should be brought into contact, and the rubber tubing wired or tied to the glass tube. The portion of the rubber tube between the wire or string should be shellacked. Only in this manner can an absolutely tight and impervious joint be secured. When weighed U-tubes are disconnected from the other tubes, the ends should be closed with short pieces of rubber tubing closed at one end by glass plugs. These stoppers should be removed while weighing the tubes.

EXERCISE 9.

Determination of Water of Crystallization in Magnesium Sulphate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

Fill three Marshand tubes with calcium chloride as directed in the preceding section. Shellac the exposed parts of the rubber or cork stoppers. Connect these tubes with a hard-glass bulb as shown in Fig. 9, and support the series so that the bulb-tube may be heated by means of a Bunsen burner. A Bunsen filter-pump or a large bottle filled with water having an exit at the bottom for the water, or a siphon extending to the bottom of the bottle and a second tube passing through the stopper at the top for entrance of air, should be provided to draw air through the apparatus. A wash-bottle containing concentrated sulphuric acid should be inserted between the last U-tube and the aspirator. All joints made by rubber tubing should have the glass tubes in contact and the rubber tubes should be wired or tied to the glass and the part between should be shellacked. After the

apparatus has been set up the first calcium-chloride tube should be closed by a rubber tube and glass plug. Gentle suction should be applied so

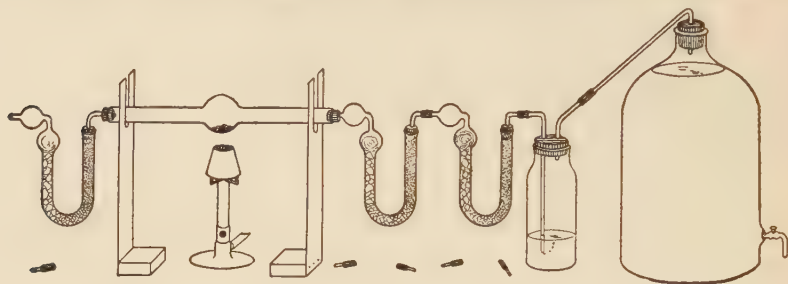


FIG. 9.

that on disconnecting with the aspirator, the acid in the wash-bottle shall rise in the long glass tube, showing a partial vacuum in the apparatus. The height of this acid should be carefully noted, and if an appreciable change occurs in five minutes, a leak exists in some of the joints, which must be found and closed before proceeding with the analysis. When the apparatus has been made air-tight, light the Bunsen burner and heat the bulb-tube to redness and draw air slowly through the apparatus for about one-half hour. The U-tubes to the right of the bulb-tube are now disconnected and weighed after being carefully cleaned. In the meantime, the bulb-tube must be closed with a rubber stopper.

The magnesium sulphate should be weighed out in a glass tube of about 5 mm. internal diameter and about 8 cm. long, which has been closed at one end. This tube is weighed, about one-half gram of the salt placed in it, and again carefully weighed. Another piece of glass tubing of the same diameter and of sufficient length is taken, and the weighing-tube containing the salt fastened to it by means of a short piece of rubber tubing of suitable size. By means of this handle, the weighed tube is introduced into the bulb, and by tapping the glass-tube the salt is deposited in the bulb, as shown in Fig. 10. The tube is carefully withdrawn so as not to drop any

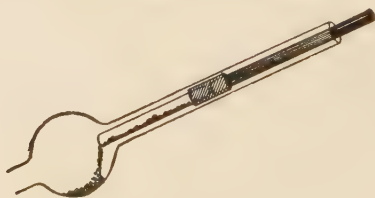


FIG. 10.

adhering particles of salt, the weighed tube carefully detached from the rubber connector and again accurately weighed with whatever magnesium sulphate is left adhering to it. The difference between the last two weights gives the weight of magnesium sulphate deposited in the bulb-tube. The

weighed U-tubes are connected in position again and the apparatus once more tested for leaks. If none are found, the bulb-tube is gently heated by means of the Bunsen burner, while a slow current of air is drawn through the tubes. If the U-tubes become appreciably warm from the heat of the Bunsen burners, they must be shielded from the heat by means of asbestos boards or other non-conducting material. Finally, when the moisture which condenses in the bulb has been removed by the current of air, the bulb is heated to dull redness for about fifteen minutes. The burner is then removed, the weighed U-tubes disconnected and weighed again. As soon as the U-tube is removed, the bulb-tube is closed with a rubber stopper. It is then replaced and the heating continued for about half an hour and the U-tubes again weighed. This process is repeated until the U-tubes no longer increase in weight. The percentage of water is calculated from the weight of magnesium sulphate taken and the increase in weight of the U-tubes.

DETERMINATION OF METALS.

CHAPTER IV.

DETERMINATION OF METALS AS OXIDE.

46. Properties of Weighable Precipitates.—In Chapter II mention was made of some of the properties of a salt or other combination of an element which determine its availability for the separation of that element from the solution. The discussion was limited to the requirements of complete precipitation and thorough washing. In other words, all of the element to be determined must be present in the precipitate, and all other substances must be removed from the precipitate. It is then in condition to be weighed as such. Generally the element forms part of a more or less complex chemical compound—oxides, chlorides, and sulphates being common forms in which elements are weighed. This compound must be of *definite composition*, so that the percentage of the element to be determined is *fixed* and *invariable*. The weighed substance must be *non-volatile*, *not strongly hygroscopic*, and in general unacted on by the atmosphere or the fumes liable to be present in the laboratory. Other things being equal, a precipitate of simple composition is apt to be of constant composition, and therefore suitable for weighing.

47. Properties of the Metallic Oxides.—The oxides of the metals have been found in many cases to possess all the properties essential to a weighable compound. The affinity of most elements for oxygen is so strong that even on ignition this element is not expelled. The oxygen of the air will even reoxidize most metals if they have become reduced by carbon or reducing-gases. The almost universal solvent in which precipitations are made is water which is composed of oxygen to the extent of about 89%. If a metal is to be *weighed* as an OXIDE, it may be *precipitated* as

HYDROXIDE, CARBONATE, OR OXALATE. In the case of many metals the salts of volatile acids may be ignited, leaving the metal as oxide. This method is especially applicable to nitrates and organic salts. In some cases the salts of non-volatile acids may be converted into oxides by heating with ammonium carbonate or mercuric oxide, the acid being driven off in combination as the volatile mercury or ammonium salt. These various methods will now be studied in detail, the metals being considered in groups in which the method of analysis is nearly identical for each group.

IRON, ALUMINIUM, AND CHROMIUM GROUP.

METAL PRECIPITATED AS HYDROXIDE BY AMMONIUM HYDROXIDE AND WEIGHED AS OXIDE.

48. Precipitation of the Hydroxides of Iron, Aluminium, and Chromium.—The hydroxides of these three metals are almost entirely insoluble in water, either hot or cold. They differ markedly in their solubilities in alkali. Iron is almost absolutely insoluble in ammonia or the fixed alkalies, while aluminium is easily soluble in the fixed alkalies and slightly so in ammonia. Chromium occupies an intermediate position in this respect between iron and aluminium, being almost insoluble in ammonia and moderately soluble in the fixed alkalies.

Iron may, therefore, be completely precipitated by sodium, potassium, or ammonium hydroxide. It is found, however, that ferric hydrate carries down some of the potassium or sodium which cannot be washed out. Ammonium hydroxide is, therefore, always used in precipitating iron, which for this purpose must be in the *ferric* condition. Any ferrous iron may be converted into ferric by boiling the solution after the addition of a few drops of nitric acid or bromine-water.

As chromium and aluminium are soluble in sodium hydroxide, these metals are also precipitated by ammonium hydroxide. As aluminium hydroxide is soluble in even a slight excess of ammonia, the solution must be made as nearly *neutral* as possible. Ammonium chloride greatly weakens the alkaline properties of ammonia, and for this reason a considerable amount of this salt

is added to the solution of aluminium. This is unnecessary in the case of chromium and iron, because of their insolubility in ammonium hydroxide.

Chromium hydroxide dissolves slightly in ammonium hydroxide in the cold, but is completely precipitated on boiling. Chromium must be in the *chromic* or *basic* condition. Chromates are reduced to chromic compounds by adding sodium sulphite to the solution acidified with hydrochloric acid, or, still better, by passing in gaseous sulphur dioxide.

49. Washing.—The hydroxides of these three metals are gelatinous, and therefore there is no danger of their passing through the paper. They clog the pores, however, so that rapid filtration and washing can be accomplished only by using suction or a hot-water funnel. The washing must be thorough, as any ammonium chloride left in the precipitate reacts with the hydroxides, liberating ammonia and forming a chloride of the metal which volatilizes so that the result obtained is low. When these hydroxides dry they shrivel and crack so that if the washing is discontinued for a short time fissures are produced in the precipitate, through which the water passes without taking the impurities out of the precipitate. If the washing must be discontinued, the stem of the funnel should be closed with a piece of rubber tubing and a glass plug and the funnel filled with water. Many of these difficulties may be overcome by using paper pulp, as described on page 27.

50. Ignition of the Filter-paper.—When the filter-paper is burned neither the aluminium nor the chromium hydroxides are reduced by the hot carbon. Ferric hydroxide, however, is partly reduced to the magnetic oxide of iron, Fe_3O_4 , while the remainder is converted into ferric oxide, Fe_2O_3 . As much of the precipitate as possible should therefore be detached from the paper, so that the error from this source may be negligible. If the filter-paper, with whatever ferric hydroxide cannot be removed, is burned in the platinum crucible, the iron which is reduced is apt to alloy with the platinum and be difficult of removal. It should, therefore, be burned in the flame of the Bunsen burner while held by a platinum wire. If a more open platinum dish, such as is used in milk analysis, is at hand, the moist precipitate may be

placed in the dish with the apex of the filter-paper on top. The side of the dish is now heated so that the paper dries and finally burns. The access of the air to the paper is so good that little iron is reduced.

51. Contamination of the Precipitate with Silica.—It is very difficult to obtain precipitates of these three metals which are free from silica. The ammonia which is used as a precipitant almost invariably contains silica which has been derived from the reagent bottle, most of which is precipitated and can be filtered off. Appreciable amounts of silica are obtained by the disintegration of the glass of the beaker in which the metal is precipitated. This silica is filtered off and weighed with the precipitate. *The digestion of the alkaline solution should, therefore, be as brief as possible, and the excess of ammonia as small as possible.* If too much ammonia is added it should be neutralized with dilute hydrochloric acid. It is also better to conduct the precipitation in a porcelain dish, since porcelain is less easily attacked by alkalis than glass. If a platinum dish is available, this source of error is entirely avoided. If glass is used the error from this source may be reduced, by working rapidly, to almost negligible quantities of .1 or .2%. If Jena beakers are used the error is still less.

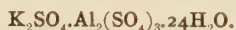
If the highest degree of accuracy is desired the percentage of silica must be determined and a correction made on the weight of the original precipitate. This determination is carried out by dissolving the precipitate in acid, evaporating to dryness on the water-bath, redissolving in acid and water, and filtering off the silica, which is washed, ignited, and weighed. For this purpose the iron precipitate may be dissolved by digesting the powdered material with hydrochloric acid. Aluminium oxide may be dissolved in the same manner, but the action is very slow unless paper pulp is used during the precipitation, as directed on page 27. It dissolves more easily if first heated with eight parts of concentrated sulphuric acid and three parts of water, and then water added. It is also rendered soluble by fusion with potassium bisulphate. This method is especially to be recommended for both iron and aluminium, because the silica may be rendered insoluble by dissolving the melt in dilute sulphuric acid and evaporating until fumes of sulphuric acid are evolved. Chromium oxide is best dissolved by fusion in the platinum crucible with sodium carbo-

nate and potassium nitrate, potassium chromate being formed. This solution must be acidified with hydrochloric acid and evaporated to dryness and the silica determined as in the other oxides.

52. Removal of Organic Material.—These metals are not completely precipitated if organic matter is present in the solution. It may be detected and also removed by evaporating the solution to dryness and igniting. This is not applicable if chlorides are present. In that case boiling with concentrated nitric acid or potassium chlorate and hydrochloric acid must be resorted to. The solution may also be treated with excess of sulphuric acid and evaporated to dryness and ignited. If the amount of organic matter is small, the ignition will frequently be unnecessary, as the charred material will be entirely destroyed by the concentrated sulphuric acid produced by the evaporation. A few drops of nitric acid followed by heating the solution will render it clear more quickly.

EXERCISE 10.

Determination of Aluminium in Potash Alum,



Weigh carefully 2 grams of pure recrystallized potash alum. If balanced watch-crystals are used, place them on the scale-pans and ascertain if the pointer indicates zero when the beam and pans are released. If it does not, balance the watch-crystals by means of a small weight or the rider. Place a 2-gram weight on the right-hand watch-crystal and weigh out 2 grams of the alum as directed in Exercise 4. Transfer to a 500-c. beaker, brushing off the watch-crystal with a clean camel's-hair brush, and dissolve in 200 c.c. of water. Add about 50 c.c. of ammonium chloride solution, which should be filtered if not perfectly clear. The ammonium chloride may also be introduced together with paper pulp by adding 15 c.c. of concentrated hydrochloric acid to two or three *ashless filter-papers* * and 25 c.c. of dilute ammonia. Warm on a hot plate or an asbestos board or wire gauze over a Bunsen burner. Add filtered dilute ammonia with constant and vigorous stirring of the solution until the odor of ammonia can be detected after vigorous stirring. Red litmus-paper should be only slowly turned blue when held over the solution. If too much ammonia has been added it should be nearly neutralized with dilute hydrochloric acid.

* The weight of the ash of this paper is stated on the package obtained from the dealers in chemical apparatus and is usually small enough to be neglected. The paper should be kept in a box or other receptacle where it can be kept perfectly clean.

53. Washing and Transferring the Precipitate to the Filter-paper.—After the solution has thus been made faintly alkaline, heat it nearly to the boiling-point for a few minutes. Fit a funnel with an *ashless filter-paper* preparatory to filtering by suction as directed in Chapter II. An 11 or 12½ cm. filter-paper should be used and the funnel should be of such a size that a space at least a quarter of an inch is left free above the paper. Allow the precipitate to settle a few minutes and then decant the clear liquid through the paper, using suction. Guide the stream of water by holding the stirring-rod against the lip of the beaker. Add about 75 c.c. of hot water from the wash-bottle,* which for this purpose is kept on a steam-bath or hot plate. Stir the precipitate well with the stream of water. For this purpose the jet of water must be quite large and care must be taken not to spatter the precipitate out of the beaker. Allow the precipitate to settle and decant through the funnel as before. Repeat the washing by decantation twice and then transfer the main precipitate to the funnel. Holding the stirring-rod against the beaker with the left hand, sweep the precipitate from the beaker by means of a stream of water from the wash-bottle, which is held in the right hand as shown in Fig. 11. When the

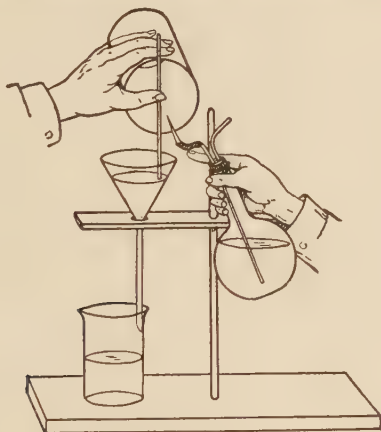


FIG. 11.

bulk of the precipitate has been transferred in this manner, the particles adhering firmly to the glass must be removed by means of a so-called *police-man*, which is made by inserting the end of a rather large-sized stirring-rod

* A so-called hot-water wash-bottle is prepared by fastening asbestos paper, a sheet of cork, or other insulating material around the neck of an ordinary wash-bottle by means of pieces of wire or string. A thick cord closely wound around the neck of the flask will serve the same purpose. The water should not be allowed to boil or steam will enter the mouth when blowing out the water. To overcome this difficulty, a piece of rubber tubing should be placed on the glass tube which enters the mouth. By closing this tube with the teeth when not blowing, steam is kept out of the mouth.

into a short piece of rubber tubing. The rubber tube should be left projecting slightly beyond the end of the glass tube and sealed together with a little bicycle cement.

The bottom as well as the sides of the beaker must be rubbed clean with this policeman. Both the stirring-rod and the policeman must finally be freed from particles of the precipitate. If portions of the precipitate cannot be rubbed off the glass they should be dissolved in a few drops of dilute hydrochloric acid and reprecipitated by neutralizing with ammonia and warming the solution. When all of the precipitate has been transferred to the funnel, it is washed with hot distilled water until free from chlorides. The exposed portion of the filter-paper must also be well washed. Test the wash-water from time to time with nitric acid and silver nitrate, finally using several cubic centimeters. In washing this precipitate, care must be taken that all of the water is not sucked off the precipitate so that it cracks, producing fissures through which the wash-water passes without dissolving the ammonium chloride. If for any reason the washing must be discontinued, the stem of the funnel should be closed with a short piece of rubber tubing and a glass plug and the funnel filled with water.

54. Ignition and Weighing of the Precipitate.—During the washing of the precipitate a platinum crucible with the lid is supported on a clean pipe-stem or platinum triangle resting on a tripod and heated to redness with a Bunsen burner. The air-vents of the Bunsen burner are adjusted so that the flame is entirely colorless. The crucible must be kept well above the inner cone. While still red-hot the crucible is seized with a clean pair of forceps or crucible tongs and placed in a desiccator, which, for this purpose, is provided with a pipe-stem or glass triangle. After fifteen minutes it is weighed, the weight being recorded on the right-hand side of the NOTE-BOOK, the page being *fully labelled and dated*. The left-hand page is reserved for a brief description of the process of analysis, and especially any procedure which led to disaster or failure and the remedy adopted. All of this work should be done during the intervals when the liquid is running through the funnel. It will run just as fast if not watched.

The moist precipitate with the paper is taken out of the funnel and transferred to the weighed platinum crucible. If there is any delay, so that the precipitate is partially dried, it must be placed in the steam-oven and completely dried. It then shrinks to a very small bulk. The lid of the crucible must in this case be very carefully placed on the crucible, as a little moisture left in the hard lumps of the precipitate forms steam and scatters the precipitate with considerable force. When burning the moist precipitate, the paper is placed in the crucible with the apex up, so that spattering during drying will not throw the precipitate out of the crucible. Any portions of the precipitate left on the funnel are wiped off with small pieces of quantitative filter-paper and placed in the crucible. The covered crucible is then placed on the triangle and heated with a very small flame

until steam and volatile matter cease to escape. The heat is gradually increased until the water and most of the volatile matter are expelled from the precipitate and the paper. The lid is now taken off the crucible, which is placed on its side and heated with the full flame of the Bunsen burner. As the carbon burns, the crucible is turned to expose fresh portions to the action of the air. The crucible is finally heated with the blast-lamp until the aluminium oxide is perfectly white. While still red-hot, the crucible is transferred to the desiccator and after fifteen minutes, weighed. The crucible is again heated in the blast-lamp, cooled in the desiccator, and weighed. This is repeated until the weight is constant within .2 or .3 milligram.

The percentage of Al_2O_3 found is calculated by dividing the weight of the precipitate by the weight of alum taken and multiplying the result by 100. The theoretical percentage of Al_2O_3 in potash alum is 10.76. If a result much higher than this is obtained, the precipitate may be contaminated with silica, which is determined as directed in the next exercise, with the exception that grinding the precipitate will be unnecessary if paper pulp has been used during the precipitation.

EXERCISE II.

Determination of Iron in Soft-iron Wire.*

In this exercise the determination should be carried out in duplicate, the two analyses being carried on side by side.

Clean the wire thoroughly by rubbing with emery-cloth or sandpaper until all rust is removed and finally wiping with filter-paper. The wire should be wound in a spiral around a lead-pencil and should not be touched with the fingers after being wiped with the filter-paper. Weigh out from 200 to 300 milligrams of the wire and transfer to a 200-c.c. beaker. Add 5 c.c. of concentrated nitric acid and a little water. Cover the beaker with a watch-crystal and warm on the hot plate under the hood. When the iron is all dissolved, rinse off the watch-crystal with a little distilled water and evaporate to dryness on the hot plate. Add 10 c.c. of dilute hydrochloric acid and again evaporate to dryness on the water-bath. After the ferric chloride is dry, heat for one-half hour on the water-bath, dissolve in a few cubic centimeters of dilute hydrochloric acid, add a little water, and filter off the silica on a small filter-paper. Wash the paper free from iron with hot distilled water to which a little hydrochloric acid has been added. The volume of the filtrate should be about 200 c.c.

It is best to precipitate the iron in a platinum dish. If such a dish is not available, an evaporating-dish of Berlin porcelain should be used or a

*This wire is such as is used in standardizing potassium permanganate or other oxidizing solutions and is sold for use as piano-strings, and to florists for making wreaths.

Jena beaker. The solution is neutralized with filtered ammonia, and brought to a boil. After allowing the precipitate to settle for a few minutes, the clear liquid is decanted through a 12½ or 15-cm. ashless filter-paper arranged for suction as described in Chapter II. The precipitate is washed twice by decantation and then transferred to the funnel and washed with hot water, observing the precautions given in Exercise 10. Toward the end of the washing the stream of water from the wash-bottle should be so directed as to loosen the precipitate from the sides of the paper and wash it down into the point of the funnel. When the precipitate has been washed *free from chlorides* it is dried in the steam- or air-oven. The temperature of the latter should not be allowed to rise much above 100°Centigrade.

55. Ignition of the Paper on Platinum Wire.—A piece of glazed paper, preferably of a light color, about 8×10 inches is spread out on the desk. A small camel's-hair brush, a piece of platinum wire about 4 inches long fastened to a glass or other handle, a Bunsen burner with a long blue flame, the ignited and weighed platinum crucible and the dried precipitate in the funnel are brought together. The glazed paper is carefully brushed clean with the camel's-hair brush. The crucible is placed in the center of the paper. The paper is taken out of the funnel and the precipitate loosened with the platinum wire and dropped into the crucible. Very little of the precipitate should be left on the paper. Rubbing the two inner surfaces of the filter-paper together will sometimes loosen a considerable amount of the precipitate. If any portion of the precipitate is found adhering to the funnel it should be rubbed off with a small piece of ashless filter-paper which has been moistened with a little dilute nitric acid. The filter-paper is now folded as if to be inserted into a funnel. It is rolled up tightly on one of its edges and the platinum wire is wrapped around the upper part of the paper which is always freest from portions of the precipitate. It is now held by means of the handle of the platinum wire over the crucible and the point touched to the Bunsen burner flame and ignited. The charred paper is completely burned by holding it in the oxidizing flame of the Bunsen burner and then exposing the red-hot carbon to the oxygen of the air. The ash is allowed to drop into the crucible. The wire is now brushed off, the crucible is taken in the left hand and any particles which have fallen on the paper are brushed into it. The crucible is placed on its side on a pipe-stem triangle and heated with the Bunsen burner until any unburned carbon of the filter-paper is oxidized.

If a platinum dish is available the moist precipitate with the apex up may be placed in the dish which is gently heated on one side with the Bunsen burner. When the paper is completely charred the dish may be heated to redness until the carbon is completely burned. The precipitate is then heated with the blast lamp for a few minutes, cooled in the desiccator and weighed. It is re-ignited and weighed until the weight is constant.

56. Calculation.—The weight of Fe_2O_3 multiplied by the percentage of iron in Fe_2O_3 (70 per cent) gives the weight of iron found. This number multiplied by 100 and divided by the weight of iron taken gives the percentage of iron in the wire which is usually 99.6 to 99.8 per cent. The result may also be computed by logarithms. The log. of the weight of the precipitate is added to the log. of the percentage of iron in Fe_2O_3 . From this sum is subtracted the log. of the weight of iron wire taken. This log. + 2.0 gives the log. of the percentage of iron in the wire. The duplicates in this analysis should agree within .1 to .2 per cent. If they vary more than this amount a third or even a fourth analysis must be made.

57. Determination of Silica.—If the percentage found is greater than 99.8 per cent, the error is probably due to silica, especially if the precipitation was carried out in a beaker. Instead of making another determination, the percentage of silica should be determined and a correction made on the percentage found. For this purpose the precipitate is ground quite fine in an agate mortar. Loss by spattering should be avoided by covering the mortar with a piece of paper through which the pestle passes. When as much of the precipitate as can be readily removed from the crucible has been ground, the pulverized material is returned to the crucible which is then weighed. The difference between this weight and the weight of the crucible gives the weight of the iron oxide taken for the silica determination. The loose material is transferred to a 100-c.c. beaker, 15 c.c. concentrated hydrochloric acid and 10 c.c. water added. The beaker is digested on the hot plate until the iron is dissolved. A little acid is also added to the crucible which is also heated until the iron is dissolved. This solution is added to that in the beaker. The beaker is now placed on the water-bath and the solution evaporated to dryness and heated dry for one-half hour. Dilute hydrochloric acid is added and the heating continued until the iron is again dissolved.

The powdered precipitate, after being weighed in the crucible, may also be fused with acid potassium sulphate. The burner should be turned down until the heat is just sufficient to keep the material fused. When the iron is all dissolved the crucible is allowed to cool, transferred to a beaker and the melt extracted with dilute sulphuric acid and the solution evaporated until fumes of sulphuric acid are evolved.

The solution obtained by either method is filtered through an ashless filter-paper, the silica in the beaker being transferred to the paper by means of a policeman as described in Exercise 10. The silica is washed and, after burning the paper, is ignited, finally for a few minutes with the blast-lamp. The crucible is cooled in the desiccator and weighed. The contents of the crucible should be pure white, any tinge of red indicating iron due to imperfect washing or undissolved ferric oxide. On adding a little pure hydrofluoric acid the precipitate should be entirely volatilized on heating. Any residue which, on repeated treatment with

hydrofluoric acid, fails to volatilize is not silica. As only part of the original iron precipitate was taken for this analysis the amount of silica in the entire precipitate must be calculated and deducted to give the true weight of Fe_2O_3 from which the percentage of iron in the iron wire must be re-calculated, as in the following illustration. 0.3350 gram of the iron wire was weighed out. 0.4820 gram of the ferric oxide was obtained. The percentage of iron calculated from this weight of oxide by the method already given is 100.7. After grinding the precipitate for the silica determination, 0.4153 gram remained in which .0043 gram SiO_2 was found. The amount present in the entire precipitate was obtained from the proportion $0.4135 : .0043 :: 0.482 : x$ where $x = .0050$. On subtracting the silica from the weight of the impure precipitate we obtain 0.4770 as the weight of ferric oxide. On recalculating the percentage of iron we obtain 99.68.

DETERMINATION OF COPPER, MANGANESE, NICKEL, AND COBALT BY PRECIPITATION WITH CAUSTIC ALKALI.

58. Precipitation and Washing.—A number of metals cannot be precipitated as hydroxide with ammonia, because of their solubility in ammonium salts. Some of these metals form hydroxides which are insoluble in sodium and potassium hydroxides, and may be precipitated by either of these reagents. Considerable difficulty is experienced in completely washing out the excess of alkali from the precipitate and, unlike ammonia, it is not expelled by ignition. On digesting the ignited precipitate with water the alkali can frequently be detected by its alkaline reaction. By filtering, washing, and reigniting, a considerable loss in weight is frequently noted.

The solution should be dilute and only a slight excess of alkali added. The liability of contamination of the precipitate with silica from the action of the alkali on the glass, which was met with in the determination of iron, aluminium, and chromium is still more pronounced when the stronger alkalis are used. The precipitation should therefore never be carried out in glass. Porcelain or, wherever possible, platinum dishes should be used. The precipitate should be tested for the presence of silica by solution in hydrochloric acid, evaporation to dryness, again dissolv-

ing in acid, filtering, washing, and weighing the residue as directed under iron. These oxides dissolve with ease in acid.

59. Composition of the Ignited Oxides.—Considerable difficulty is experienced in obtaining precipitates of constant composition. CUPRIC HYDROXIDE is converted on ignition into cupric oxide, CuO , but if reduced by the filter-paper or reducing gases from the flame to metallic copper it reoxidizes to cuprous oxide, Cu_2O . This is converted into cupric oxide by moistening with nitric acid, evaporating to dryness and igniting.

MANGANESE HYDROXIDE is oxidized by the oxygen of the air even at the ordinary temperature. It is not reduced either by the carbon of the filter-paper or by the reducing gases of the flame. On ignition in presence of air it is converted into manganoso-manganic oxide, Mn_3O_4 . It is impossible, however, to obtain a precipitate in which the percentage of manganese corresponds to the theoretical for Mn_3O_4 . Pickering has shown that the amount of manganese in the ignited oxide varies from 69.688 to 74.997%, according to the temperature to which the oxide has been heated and other undetermined conditions. For this reason only *small* amounts of manganese should be weighed as Mn_3O_4 .

When COBALTOUS HYDROXIDE is heated in contact with the solution from which it was precipitated, it is gradually converted by the oxygen of the air into cobaltoso-cobaltic hydroxide. On drying, it absorbs more oxygen, but on strong ignition oxygen is driven off, leaving cobaltous oxide CoO . On cooling in contact with the air, oxygen is again absorbed, the light brown cobaltous oxide changing more or less completely to the black cobaltoso-cobaltic oxide Co_3O_4 . If the air is excluded by a current of carbon dioxide this action is prevented, and the pure cobaltous oxide is obtained. This oxide is readily reduced to metallic cobalt by ignition in a stream of hydrogen and the alkali which could not be completely removed by washing the hydroxide can now be quite readily extracted with hot water.

NICKELOUS HYDROXIDE is converted on ignition into nickelous oxide NiO , which is unaltered on heating in the air. It is readily reduced to metallic nickel on ignition in a stream of hydrogen or of carbon monoxide.

EXERCISE 12.

**Determination of Copper in Crystallized Copper Sulphate,
 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.**

Weigh out 1 gram of the pure salt, transfer to a platinum or porcelain dish, and dissolve in about 200 c.c. of distilled water. Make a dilute solution of caustic soda by dissolving about 1 gram in 25 c.c. distilled water. Heat the copper solution nearly to boiling and add the caustic-soda solution with constant stirring until no further precipitation occurs. Allow to settle for a few minutes, then decant through a paper fitted into a funnel for suction. Wash the precipitate twice by decantation with hot water, then transfer to the funnel and complete the washing with hot water until the wash-water is perfectly neutral. Dry the precipitate in the funnel at 100°C . Remove the precipitate from the paper as directed in Exercise 11 and place it on a watch-crystal. Burn the paper on the platinum wire, being careful to wrap the wire around a portion of the paper on which there is the least amount of precipitate. Let the ash fall into a porcelain crucible. Add a few drops of concentrated nitric acid, place the lid on the crucible, and evaporate off the excess of acid with a very small flame of the Bunsen burner, finally heating quite strongly. If any carbon from the filter-paper remains unburned, repeat the treatment with nitric acid. When the crucible is cold set it on the glazed paper and transfer the main portion of the precipitate to the crucible, brushing the watch-crystal and paper thoroughly. The moist paper with the precipitate may also be placed in the crucible and the paper burned as directed in Exercise 10. The precipitate must be moistened with nitric acid as directed for the ash of the filter-paper. Finally heat the crucible with the full flame of the Bunsen burner for ten or fifteen minutes, cool in the desiccator, and weigh. As copper oxide is hygroscopic, the weight should be taken rapidly. The crucible is reheated and when weighed the second time the weights should be placed on the right-hand pan before the crucible is placed on the left-hand pan so as to make the final adjustment with the rider or by taking the swings of the pointer before the precipitate gains appreciably in weight. The percentage of copper found in copper sulphate should be within .1 or .2 per cent of the theoretical 25.46 per cent. The method gives high results.

EXERCISE 13.

**Determination of Nickel in Nickel-ammonium Sulphate,
 $(\text{NH}_4)_2\text{SO}_4 \cdot \text{NiSO}_4 \cdot 6\text{H}_2\text{O}$.**

Weigh out 2 grams of crystallized nickel-ammonium sulphate and transfer to a porcelain dish. Dissolve in about 200 c.c. distilled water. Heat nearly to boiling and add, with stirring, a dilute but freshly made solution of caustic soda until precipitation is complete. Continue heating the solution for ten or fifteen minutes. Wash by decantation two or three times, then wash thoroughly with hot water on the filter-paper. Dry the pre-

precipitate, detach from the paper, and place it on a watch-crystal. Burn the filter-paper over the porcelain crucible. Treat the residue with a drop of concentrated nitric acid, evaporating off the excess. Add the remainder of the precipitate and heat with the Bunsen burner to constant weight. The precipitate should now be examined for alkali by digesting with hot water and testing with litmus. If alkali is present it is removed by repeated extraction with hot water, the precipitate being finally heated to constant weight again. Calculate the percentage of nickel found in the nickel-ammonium sulphate. Theoretical percentage is 14.86.

The nickel oxide may also be converted into metallic nickel by heating in a stream of hydrogen. For this purpose the perforated lid and porcelain stem of the Rose crucible are most convenient. In place of this an ordinary clay pipe may be used. The hydrogen from a Kipp generator should be freed from arsine by passing it through a mercuric chloride solution and dried by passing through calcium chloride or concentrated sulphuric acid. The apparatus is set up as shown in Fig. 12. The stream of hydrogen should be passed for a few minutes to displace the air from the wash-bottle and the U-tube. An explosion will not pass through the

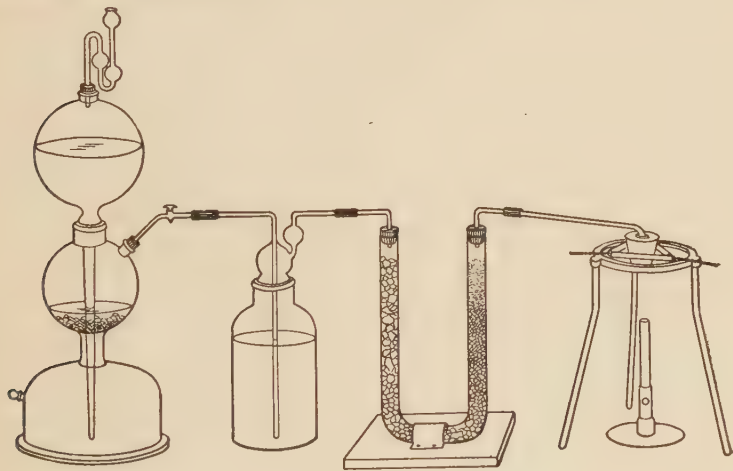


FIG. 12.

apparatus if a plug of cotton or glass wool is placed in the glass tube or limb of the U-tube nearest the crucible. The crucible is then gently heated with a small flame from a Bunsen burner, which is turned on full after a few minutes. The crucible is finally allowed to become nearly cold in the stream of hydrogen. It is then transferred to the desiccator for a few minutes before weighing. The ignition in the stream of hydrogen is repeated until the weight is constant. The precipitate is then tested for silica by dissolving the metal in a little dilute nitric acid. If any silica is found, it is filtered off, washed, and weighed.

CHAPTER V.

DETERMINATION OF METALS AS OXIDE.

PRECIPITATION OF LEAD, BISMUTH, CALCIUM, BARIUM, AND STRONTIUM BY AMMONIUM CARBONATE.

60. Precipitation by Ammonium Carbonate.—Some of those metals whose oxides or hydroxides are soluble in water or in solutions of the alkali hydroxides may be precipitated by ammonium or sodium carbonate. Ammonium carbonate cannot be used with some of the metals because the precipitate dissolves, forming a double salt with the ammonium compounds produced by the neutralization of the mineral acid with which the base was combined. Ammonium carbonate is used in preference to sodium or potassium carbonate, because of the greater ease of freeing the precipitate from the ammonium salts by washing or volatilization during ignition. On the other hand, some carbonates of the metals which can be precipitated by ammonium carbonate form acid carbonates which are slightly soluble. Ammonium carbonate as obtained either in the solid form or in solution almost invariably contains acid ammonium carbonate. Free ammonia must therefore always be added to the solution to be precipitated. The precipitation is therefore usually said to be made by *ammonia* and *ammonium carbonate*, by the latter term being designated the commercial article.

61. Conversion of the Carbonate into the Oxide.—The ease of converting the carbonates of these metals into oxides varies greatly. *Lead carbonate* loses all of its carbon dioxide below red heat; indeed at the ordinary temperature part of it passes off so that the precipitate formed by ammonia and ammonium carbonate is a basic lead carbonate. In the case of the alkaline-earth metals the precipitate formed in each case is the normal carbonate, and it may be dried and weighed as such. *Calcium carbonate* may be

completely converted by the heat of the blast-lamp into calcium oxide, so that this metal may be weighed either as the oxide or as the carbonate. It is impossible to completely convert *strontium* or *barium carbonates* into oxides. These metals are, therefore, weighed as carbonates.*

AS LEAD SALTS are very easily reduced to the metallic form, the bulk of the lead precipitate must be removed from the filter-paper before the latter is burned. The lead which remains on the paper is reduced to metal, and must be reconverted to oxide by treatment with concentrated nitric acid and ignition of the lead nitrate formed. The bulk of the lead precipitate is then placed in the crucible and by ignition converted into the monoxide of lead.

If it is desired to weigh the CALCIUM AS OXIDE, the precipitate need not be dried or removed from the filter-paper, but is introduced into the crucible, dried by gentle heat, ignited with access of air to burn the paper, and finally heated with the blast-lamp to constant weight. This is, therefore, the simplest and most rapid method of weighing calcium. It has the disadvantage, however, that the calcium oxide is very hygroscopic, and when moist absorbs carbon dioxide from the air. The precipitate must, therefore, be weighed as quickly as possible.

CALCIUM CARBONATE is stable in the air and may, therefore, be weighed with the greatest accuracy. If the precipitate is to be weighed as carbonate, it must be dried and removed from the paper. This is not difficult, as it forms a loose powder on drying. It is placed on a watch-crystal, while the paper is burned in the crucible or on a platinum wire. By this treatment the calcium remaining on the paper is converted into oxide, which must be changed to carbonate. This is accomplished by sprinkling some dry powdered ammonium carbonate on the calcium oxide, moistening with a drop or two of water, and heating very gently to drive off the excess of ammonium carbonate and water. This operation is repeated, then the bulk of the precipitate is added, which is also heated gently with the Bunsen burner. After weighing the precipitate, it must be treated with ammonium

* Calcium carbonate decomposes at 825° , strontium carbonate at 1155° , and barium carbonate at 1450° .

carbonate and a little water and again heated and weighed, to ascertain if the weight is constant.

The precipitate of BARIUM or STRONTIUM may be thrown moist into the platinum crucible and heated with the Bunsen burner until dry and the paper burned. The hot carbon reacts with the carbonates of these metals, forming carbon monoxide and the oxide of the metal. After the complete combustion of the filter-paper, the precipitate should be treated with ammonium carbonate and water and heated to expel the excess of the reagent, finally to dull redness with the Bunsen burner.

EXERCISE 14.

Determination of Strontium in Strontium Carbonate, SrCO_3 .

Weigh out 1 gram of pure strontium carbonate. Transfer to a 400-c.c. beaker. Add 50 c.c. distilled water and dilute hydrochloric acid drop by drop with stirring or agitation of the solution until the strontium is dissolved. Dilute to 150 c.c., add a few cubic centimeters dilute filtered ammonia, then ammonium carbonate solution with constant stirring until no further precipitation occurs. Allow the beaker to stand in a warm place for several hours. Filter and wash the precipitate with water containing a little ammonia. Transfer the moist precipitate to a weighed platinum crucible. With the lid on the crucible, heat gently until the precipitate is dry. Remove the lid, place the crucible on its side, and heat strongly until the paper is burned. Cool, sprinkle some powdered ammonium carbonate over the precipitate, moisten with a little water, heat gently with the lid on the crucible until the precipitate is dry, then more strongly, but not to redness. Cool in a desiccator and weigh. Repeat until constant weight is obtained. The theoretical percentage of strontium in strontium carbonate is 59.37.

PRECIPITATION OF CALCIUM BY AMMONIUM OXALATE.

62. Calcium is almost invariably precipitated as oxalate, since this salt of calcium is more insoluble than the carbonate, while on ignition it can be converted into the carbonate or the oxide as desired. It forms a very finely divided powder when first precipitated, which gives considerable trouble by passing through the pores of the filter-paper. By digesting the precipitate with the hot solution from which it has been separated, the crystals increase in size so that after two or three hours it can be filtered without any difficulty. The same object is more quickly accomplished if the solution of calcium is brought to a boil before adding

the ammonium oxalate, which should also be hot. The solution should also be vigorously stirred during the precipitation. If the precipitate is heated very gently, it decomposes almost completely, according to the equation $\text{CaC}_2\text{O}_4 = \text{CaCO}_3 + \text{CO}$. Almost invariably, however, the calcium carbonate will be dark-colored because of the formation of some free carbon. On heating the precipitate strongly enough to cause the combustion of this carbon and thus to give it a pure-white color, a large portion of the precipitate will be converted into oxide. That portion which remains with the filter-paper will also be converted into oxide. Instead of attempting to produce the carbonate in the first instance, it is simpler to heat the precipitate with the paper from the beginning quite strongly with the Bunsen burner or the blast-lamp until it is perfectly white. It may then be brought to constant weight as calcium oxide, or it may be converted into carbonate by the addition of at least an equal bulk of ammonium carbonate, moistening with water and heating gently. This is repeated until constant weight is obtained. By weighing the calcium as oxide, the result is undoubtedly obtained more quickly, and if the weighing is done rapidly it is quite as accurate as when the calcium is weighed as carbonate. The weight of the calcium oxide may also be verified by converting it into sulphate. A few drops of sulphuric acid are added cautiously to the oxide. The excess is evaporated off on the hot plate and the calcium sulphate finally brought to constant weight by heating to redness with the Bunsen burner.

EXERCISE 15.

Determination of Calcium in Calcium Carbonate.

Weigh out 0.5 gram of pure calcium carbonate. Transfer to a 500-c.c. beaker, add a little water, and while covering the beaker with a watch-crystal add 5 c.c. dilute hydrochloric acid. When the calcium is dissolved, rinse the watch-crystal and the sides of the beaker, bringing the bulk of the solution to about 250 c.c. Neutralize with filtered ammonia, heat nearly to boiling on the hot plate, and add ammonium oxalate solution *slowly with vigorous stirring of the solution* until no further precipitation occurs. Keep the solution on the hot plate, so that it nearly boils, for several hours. Decant the clear solution through the funnel, wash with hot water by decantation several times, then transfer the precipitate to the paper

and complete the washing with hot water, testing the wash-water for chlorides. Transfer the moist precipitate to the weighed platinum crucible, dry, and burn the paper in the usual manner, finally heating with the blast-lamp for about ten minutes. Cool in a desiccator and weigh. Heat with the blast-lamp again for ten minutes and weigh, first placing the weight found necessary by the first weighing on the pan and finally taking the crucible out of the desiccator and making the final adjustment as rapidly as possible. Continue heating and weighing until constant weight is obtained.

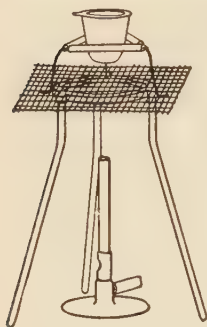


FIG. 13.

CONVERT the OXIDE into the CARBONATE by adding at least an equal bulk of powdered ammonium carbonate* and moistening with water. Place the cover on the crucible and evaporate off the water by gentle heat, then place the crucible on a pipe-stem triangle which is supported about 1 inch above a wire gauze which is heated by a Bunsen burner. Repeat this treatment, cool in the desiccator, and weigh. Continue this operation until constant weight is obtained. This weight should equal that of the carbonate weighed out for the analysis. The theoretical percentage of calcium oxide in calcium carbonate is 56.

DETERMINATION OF ZINC, MANGANESE, AND CADMIUM BY PRECIPITATION WITH SODIUM CARBONATE.

The salts of these metals readily form double salts with ammonium compounds. They cannot, therefore, be completely precipitated by sodium carbonate in the presence of considerable amounts of ammonium salts. The latter are readily removed by evaporating the solution to dryness and volatilizing the ammonium compound by gently heating the dry residue.

63. Cadmium Carbonate is almost insoluble in ammonium salts and completely insoluble in the fixed alkali carbonates and in water. On burning the filter-paper, the cadmium carbonate left upon it is reduced to metallic cadmium, which is *very volatile* at the temperature of the Bunsen burner. The precipitate should therefore be dried and removed as completely as possible from the paper. The loss of cadmium may be almost completely prevented by saturating the paper with a strong solution of ammonium nitrate, drying and igniting. The oxygen from the nitrate serves to reoxidize any cadmium which may have been reduced.

* If on volatilizing one or two grams of the ammonium carbonate a weighable residue is left, it must be purified by sublimation.

The paper during the ignition should also be held in the oxidizing zone of the Bunsen burner, for the same reason. The error may be still further reduced by first washing the paper with a little dilute nitric acid and water, and evaporating the solution to dryness in the weighed crucible. The paper may then be burned as directed previously. The precipitate is converted by ignition into oxide, which is not decomposed nor volatilized at white heat. If the precipitate is small it need not be dried, but may be immediately dissolved in nitric acid and the solution evaporated to dryness in the porcelain crucible.

64. Manganese Carbonate is quite soluble in ammonium salts. The recently precipitated carbonate is white, but on standing it becomes brown, being oxidized by the oxygen of the air. It is insoluble in solutions of potassium or sodium carbonate. On ignition in the presence of air the carbonate is converted into protosquioxide of manganese which *approximates* the formula Mn_3O_4 . Pickering has shown that the percentage of manganese in the ignited oxide varies from 69.69 to 75, according to the temperature to which the oxide has been heated. The theoretical percentage of manganese in Mn_3O_4 is 72.05. Only *small amounts* of manganese should be weighed in this form if accurate results are desired. No manganese is lost on burning the filter-paper. If the precipitate is large and not removed from the paper some difficulty will be found in securing complete combustion of the paper.

65. Zinc is precipitated as the basic carbonate. Carbon dioxide is, therefore, liberated during the reaction. The bicarbonate produced holds some of the zinc in solution, but this is completely precipitated on boiling. It is, therefore, best to precipitate the zinc from a boiling solution and keep it at this temperature for some time. If even a small amount of ammonium salts are present, the precipitation is not complete. As the boiling alkaline solution acts on glass quite energetically, it is best to use a porcelain or platinum dish. The precipitate is washed with hot water. On ignition, the carbonate is converted into oxide. In the presence of carbon or other reducing substances, both the oxide and carbonate are reduced on ignition to metallic zinc which volatilizes. The precipitate must, therefore, be treated in the same manner

as the cadmium precipitate. The zinc oxide is stable when ignited in the air in the absence of reducing agents.

EXERCISE 16.

Determination of Zinc in Zinc-ammonium Sulphate, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$.

Weigh out 2 grams of crystallized zinc-ammonium sulphate. Transfer to a platinum dish or crucible. Heat very gently with a small Bunsen burner flame or on the hot plate until the water is expelled. Keep the dish covered to prevent spattering. Increase the heat somewhat and volatilize the ammonium sulphate. When no more fumes come off, allow to cool and dissolve the zinc sulphate in water and a little hydrochloric acid if necessary. If a crucible has been used, transfer the solution to a platinum or porcelain dish, heat nearly to boiling and add with stirring a freshly made sodium carbonate solution until the zinc is entirely precipitated. Continue the heating for about fifteen minutes, allow to settle, wash several times by decantation, finally transfer to the funnel and complete the washing with hot water. Dry the precipitate, detach it from the paper and place on a watch-crystal. Replace the paper in the funnel and wash with 25 c.c. of water to which a little nitric acid has been added. Evaporate the wash-water to dryness in the weighed platinum crucible. In the meantime moisten the paper with a saturated solution of ammonium nitrate and dry in the steam-bath. Burn the paper on the platinum wire, being careful to touch it only with the oxidizing portion of a Bunsen-burner flame which is entirely free from a luminous zone. The precipitate is now transferred to the crucible and ignited with the Bunsen burner and finally with the blast-lamp. Theoretical percentage of zinc in zinc-ammonium sulphate is 16.28.

IGNITION OF SALTS OF VOLATILE ACIDS.

66. Determination of the Metals by Ignition of the Salts of Volatile Acids.—As has already been observed, it is possible to ignite the salts of many metals and obtain oxides of definite composition, from the weight of which the percentage of the metal present may be calculated. Calcium oxalate and carbonate, cadmium, manganese, zinc, and lead carbonates are examples of such salts which are obtained by precipitation. In many cases the nitrates and nitrites may be treated in this manner, but not the chlorides since they are quite volatile and the oxygen is not present to unite with the metal to form the oxide.

In some cases the oxygen may be furnished and the chlorine driven off, as a volatile compound by igniting the salt with mer-

curic oxide, nitric acid, or ammonium carbonate or nitrate. Zinc chloride may be converted into oxide by treatment with excess of mercuric oxide or nitric acid. Magnesium chloride may be converted into oxide by ignition with mercuric oxide, ammonium carbonate, or nitrate.

In the absence of substances of this character, the acid with which the metal is combined must contain oxygen and be readily decomposed and volatilized by heat. The sulphates and phosphates, though containing the necessary oxygen, are usually very stable, and the acid is with difficulty volatilized by heat.

The metals whose salts of volatile oxygen acids may be decomposed into oxides are LEAD, BISMUTH, COPPER, TIN, IRON, ALUMINIUM, CHROMIUM, MANGANESE, NICKEL, ZINC, and MAGNESIUM. No other volatile substance except the metal may be present.

67. Ignition of Salts of Organic Acids.—Many of the metallic salts of organic acids may be ignited so as to leave the metal in a weighable form. The carbon, hydrogen, nitrogen, and some of the oxygen of the organic compound are either volatilized in the free condition or combined with each other, or they unite with the oxygen of the air to form simple oxygen compounds. Most metals retain at least some of the oxygen of the organic compound, or are oxidized by the oxygen of the air. Under these conditions BARIUM, STRONTIUM, and SODIUM remain as CARBONATES with a partial reduction to oxide, which is converted to carbonate by treatment with ammonium carbonate, so that these metals are weighed as carbonates. Sodium compounds must be heated only to very low redness, because of the volatility of this metal. It is best not to attempt the complete combustion of the carbon by heat. The charred mass should be extracted with water and filtered, the solution of the sodium carbonate being evaporated to dryness in a weighed dish.

ORGANIC COMPOUNDS OF CALCIUM, MAGNESIUM, ALUMINIUM, CHROMIUM, MANGANESE, NICKEL, COPPER, LEAD, and BISMUTH may be ignited in the air until the organic matter is burned off and the oxide of the metal remains. Many organic salts froth on being heated. The crucible should therefore have a tight lid, and the heat should be applied gently at first. If this confinement is not sufficient, the crucible should be set in a larger covered cruci-

ble, since the error due to loss of metal by the mechanical carrying away of fine particles by the products of the combustion may be considerable. The ignition of the salts containing lead or bismuth must be conducted at as low a heat as possible, as these metals are readily reduced and are volatile at red heat. When the organic material is charred and the carbon ceases to burn readily the flame is removed from the crucible and ammonium nitrate added. The crucible is covered and gently heated. The ammonium nitrate fuses and oxidizes the remaining carbon and converts the metallic lead or bismuth into nitrate which is converted into oxide by red heat. Concentrated nitric acid may be used for the same purpose. When copper salts are ignited, some of the copper is left as cuprous oxide, which it is most advantageous to oxidize by igniting with mercuric oxide.

EXERCISE 17.

Determination of Lead by Ignition of Lead Nitrate, $\text{Pb}(\text{NO}_3)_2$.

Heat a porcelain crucible to redness with the Bunsen burner for ten minutes. Cool in the desiccator and weigh. Weigh out one-half gram of lead nitrate and transfer to the crucible. If the salt is in large crystals, it should be reduced to a coarse powder by grinding in a clean and dry porcelain mortar. It should be weighed out as soon as powdered. Heat gently, at first with the lid on the crucible. When decrepitation ceases and copious nitrous fumes cease to be evolved the lid may be removed. Heat to dull redness until no more fumes are evolved. Cool in the desiccator and weigh as PbO . Repeat until the weight is constant. Calculate the percentage of lead in the lead nitrate.

CHAPTER VI.

DETERMINATION OF METALS AS SULPHATE AND AS SULPHIDE.

A LARGE number of the metals form sulphates which are of definite composition and which can be heated high enough to expel all water and volatile matter without suffering decomposition. Most of the sulphates, however, are soluble. Only three, those of BARIUM, STRONTIUM, and LEAD, are insoluble enough for separation of the metal from water solution by precipitation.

68. Barium Sulphate is the most insoluble, requiring about 400,000 parts of water to dissolve one part of the salt. It is somewhat more soluble in even dilute solutions of hydrochloric acid and of ammonium chloride. It readily dissolves in concentrated sulphuric acid, especially when hot, from which it is completely precipitated by the addition of water. Barium sulphate has the very peculiar though by no means uncommon property of rendering insoluble some very soluble salts, notably the nitrates, chlorides, sulphates, and chlorates of the alkaline earths and alkali metals, ferric, aluminium, and chromic salts. Potassium salts give more trouble than sodium salts. Once carried down by the barium sulphate, these salts cannot be entirely washed out. The solution must be freed from nitrates and chlorates by evaporation with hydrochloric acid. If ferric salts are reduced to ferrous salts, iron will not be carried down by the barium sulphate. A precipitate contaminated by any of these impurities may be dissolved in concentrated sulphuric acid and reprecipitated by diluting with much water. It may also be fused with sodium carbonate, which converts the sulphate of barium into the carbonate, which may be filtered off, washed, redissolved, and reprecipitated with sulphuric acid.

It has been shown that the contamination of the precipitate

takes place at the moment of its formation. *The most favorable conditions for avoiding the contamination have been found to be a boiling-hot, slightly acid solution of large bulk, and the addition of the precipitant in very dilute solution drop by drop, and with the most vigorous stirring.* If from failure to observe any of these conditions salts are carried down, washing will not remove them. On account of its slight solubility, barium sulphate tends to come down in such a finely divided condition that it passes through the pores of the filter-paper. By precipitating as directed above and keeping the solution near the boiling-point for some time the precipitate settles out, leaving a clear solution and does not pass through the filter-paper.

On burning the paper some of the sulphate is reduced to sulphide of barium. It is customary to add a drop or two of sulphuric acid in order to reconvert the sulphide into sulphate, and then to ignite the precipitate and volatilize the excess of sulphuric acid. By this treatment barium pyrosulphate is produced, which is decomposed slowly and only at a high temperature. It has been shown that the addition of sulphuric acid is unnecessary since the barium sulphide is oxidized to sulphate by ignition in the air.

69. Strontium Sulphate is much more soluble in water and acids than barium sulphate, 1 part of the former being dissolved by about 7000 parts of cold water, and 10,000 parts of boiling water, while if the water contains sulphuric acid, from 11,000 to 12,000 parts are required. One part of the precipitate is dissolved by about 500 parts of dilute nitric or hydrochloric acid, while it is practically insoluble in 95% or absolute alcohol and in boiling ammonium sulphate solution (1 to 4). The precipitate should therefore be washed by one of the two latter solutions, or by dilute sulphuric acid. On ignition in presence of carbon or reducing gases it is converted into sulphide. This is volatile in the Bunsen burner flame, coloring it red, so that the precipitate must be detached as completely as possible from the paper. The subsequent treatment is similar to that of barium sulphate.

70. Lead Sulphate is quite insoluble in water, requiring for its solution about 23,000 parts of cold water, but if the water contains sulphuric acid 36,500 parts are required. The presence of

alcohol reduces this solubility. Solutions of ammonium salts, especially the nitrate, tartrate, and acetate dissolve lead sulphate quite readily. The two latter should be rendered strongly alkaline with ammonia. It is also dissolved by hot solutions of caustic soda or potash. Dilute nitric and hydrochloric acids dissolve considerable quantities of lead sulphate which is reprecipitated on the addition of dilute sulphuric acid. These acids are readily removed by evaporating the solution after the addition of sulphuric acid, until fumes of the latter appear. On diluting the solution with considerable water and adding alcohol, the lead is completely precipitated.

The lead precipitate should be washed by alcohol or dilute sulphuric acid, preferably by the former as the paper would char on drying if sulphuric acid were left in it, and if washed out by water some lead would be lost. On burning the paper some of the lead sulphate is reduced to metallic lead. The precipitate should therefore be removed from the paper, the latter placed in a porcelain crucible, and ignited until all carbon is burned. A drop or two of nitric acid and the same amount of sulphuric acid is added and evaporated off, care being taken to avoid spattering. The remainder of the precipitate should then be added and heated with a Bunsen burner. Sulphate of lead may very advantageously be filtered off on a Gooch crucible and dried on the hot plate.

EXERCISE 18.

Determination of Barium in Barium Chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$.

Weigh out about one-half gram of crystallized barium chloride. Transfer to a 500-c.c. beaker and dissolve in about 250 c.c. of distilled water. Heat nearly to boiling on the hot plate and add, while stirring vigorously, dilute sulphuric acid drop by drop until no further precipitate is produced. The acid may be drawn up in a glass tube or pipette and the flow of acid regulated by pressing the index finger against the upper end of the tube. After allowing the precipitate to settle a little, it can easily be seen if a drop of acid produces any precipitation. The heating of the solution is continued until the precipitate has settled completely, leaving a clear solution. About an hour is usually sufficient. It is washed several times by decantation, using about 75 c.c. of hot water each time and stirring up the precipitate thoroughly. The precipitate is transferred to the funnel and the washing with hot water continued until the wash-water is free from chlorides.

The moist precipitate with the paper may be transferred to a weighed platinum crucible or dish and ignited over the Bunsen burner with free access of air and finally over the blast-lamp. The theoretical percentage of barium in barium chloride is 56.25.

71. Determination of Metals by Evaporation with Sulphuric Acid.—Many metals form sulphates which are stable enough to be ignited and weighed, but which are soluble and therefore cannot be precipitated and washed. POTASSIUM, SODIUM, CALCIUM, MAGNESIUM, COBALT, NICKEL, and MANGANESE form such sulphates. A salt or compound of one of these metals which contains no other non-volatile metal and which contains only volatile acids may be analyzed by ignition with excess of sulphuric acid. The sulphate of the metal will remain, from the weight of which the percentage of the metal present may be calculated. In this manner the salts of nitric and nitrous acids, the halogen acids, organic acids, etc., may be analyzed.

ORGANIC SALTS of SODIUM and POTASSIUM are treated with a moderate excess of dilute sulphuric acid in a covered platinum crucible and gently heated to dull redness. The evolution of white fumes indicates an excess of sulphuric acid. The readily fusible acid sulphate of the alkali remains. Small lumps of ammonium carbonate which leave no residue on ignition are thrown into the hot crucible and the heating continued. This is repeated until the alkali sulphate no longer fuses. The crucible is cooled and weighed, and the addition of ammonium carbonate and the heating repeated until constant weight is obtained. The alkali-acid sulphate may be converted into the neutral sulphate by the application of a white heat, but some loss of the metal results.

BARIUM, STRONTIUM, and CALCIUM may be determined in salts of volatile acids by the addition of an excess of sulphuric acid, evaporating to dryness and igniting, at first gently and finally to full redness. To remove the excess of sulphuric acid, a little ammonium carbonate is sprinkled on the precipitate, which is again heated to redness. MAGNESIUM may be determined in the same manner, but a large excess of sulphuric acid should be avoided and the residue may be exposed to a moderate

red heat only or loss of sulphuric acid will result. Magnesium sulphate is very hygroscopic and must be weighed rapidly.

NICKEL, COBALT, and MANGANESE may be weighed as sulphates, but care must be exercised not to overheat, as sulphuric acid may be lost. If this has occurred, as shown by blackening of the material, dilute sulphuric acid must be added, and after evaporating off the excess the ignition is repeated. The platinum dish must not be heated above dull redness.

LEAD may be determined in organic salts, and those of volatile acids by treatment in a weighed porcelain dish or crucible with excess of dilute sulphuric acid. Loss by spattering is avoided by keeping the vessel well covered and evaporating with very gentle heat. If the residue from the ignition of an organic compound is not perfectly white, the addition of sulphuric acid and the ignition must be repeated. Lead sulphate is stable when exposed to a red heat, but reducing gases must not be allowed to come in contact with it.

EXERCISE 19.

Determination of Magnesium in Magnesium Carbonate.

Weigh one-half gram of magnesium carbonate and transfer to a weighed platinum crucible. To prevent loss by spattering expel most of the carbonic acid by heating the crucible at first gently, then strongly with the Bunsen burner, the whole operation taking about ten minutes. Allow the crucible to cool quite completely and then add about 3 c.c. dilute sulphuric acid, at first cautiously, to prevent spattering in case much carbonic acid still remains. Evaporate the solution by first heating on the hot plate and then very gently with the Bunsen burner until acid fumes cease to be evolved. If white fumes do not escape enough acid has not been added. Heat for a few minutes to dull redness, cool in the desiccator, and weigh quickly, as magnesium sulphate is hygroscopic. Repeat the ignition with the Bunsen burner until the weight is constant. The residue should dissolve completely in water and should form a neutral solution, otherwise it has been too highly heated.

Calculate the percentage of magnesium carbonate in the sample tested. Ordinary magnesium carbonate approximates the formula



DETERMINATION OF METALS AS SULPHIDE.

A large number of the metals form sulphides which are almost entirely insoluble in water, especially when it contains an excess of the precipitant. The separation of metals as sulphides from their solution is therefore very complete, and as in some cases the precipitates can be ignited as sulphides, giving very pure products, the determination of the metal as sulphide is in many cases of the highest accuracy. This is true of COPPER, ZINC, and MANGANESE.

COPPER, MERCURY, LEAD, SILVER, BISMUTH, CADMIUM, ARSENIC, ANTIMONY, and TIN may be precipitated by hydrogen sulphide from acid solutions. SILVER, CADMIUM, LEAD, and BISMUTH may also be precipitated by ammonium sulphide in alkaline solution, though the precipitation by hydrogen sulphide in moderately acid solution is generally used. LEAD and SILVER may also be precipitated by hydrogen sulphide or ammonium sulphide in neutral solution. CADMIUM may be precipitated from a potassium cyanide solution by hydrogen sulphide.

72. **Copper** may be precipitated from a neutral or slightly acid solution by ammonium sulphocyanate after reduction by sulphurous acid, ammonium sulphite, or hypophosphorous acid. The copper is precipitated as *cuprous sulphocyanate* and may be dried at 100° and weighed as such, or it may be converted into *cuprous sulphide* by ignition with sulphur in a stream of hydrogen. Many copper compounds containing no non-volatile constituent except copper may be determined by heating a weighed portion with sulphur in a stream of hydrogen, thus converting the copper into cuprous sulphide. The oxides of copper, the sulphate, nitrate, etc., may be analyzed in this manner. If the copper solution is free from oxidizing substances, it is advisable to heat it nearly to boiling before passing hydrogen sulphide, as under these conditions the precipitate collects and settles better.

73. **Washing.**—Some of the sulphides form so-called colloidal solutions with water, while others are readily oxidized, forming sulphates which dissolve in the wash-water. For this reason the wash-water must contain hydrogen sulphide, and in the case

of cadmium and arsenic hydrochloric acid should be present, more being necessary for arsenic sulphide than for cadmium sulphide.

74. Removal of Free Sulphur and Drying at 100°.—The sulphides of SILVER, MERCURY, CADMIUM, and ARSENIC cannot be ignited, but must be dried at 100° before weighing. A Gooch crucible is most advantageous for this purpose, though a weighed filter-paper may be used. As hydrogen sulphide is very readily oxidized even by the oxygen of the air, the precipitated sulphides will almost invariably contain sulphur. When the precipitate can be ignited, this contaminant does not interfere with the accuracy of the determination. When the sulphide is dried at 100° the removal of the free sulphur presents some difficulties. The solution from which the metal is to be precipitated should be freed as far as possible from oxidizing agents. The precipitation should be carried out in a cold solution, which should be protected from the air as much as possible by placing it in an Erlenmeyer flask and filtering and washing immediately after precipitation. Even under these circumstances more or less sulphur is apt to be formed, so that the precipitate should always be treated for the removal of this element. *Carbon disulphide* and a moderately strong solution of *sodium sulphite* have been used for this purpose. If carbon disulphide is used, the washed precipitate is first dried, then digested with small quantities of carbon disulphide until no sulphur is obtained by evaporating a portion of the carbon disulphide. If a Gooch crucible is used, it may be placed in a small beaker and the carbon disulphide poured over the precipitate. The precipitate may also be freed from water by washing with alcohol, after which the carbon disulphide may be added. If the sodium sulphite solution is used, the precipitate need not be dried, but must be washed thoroughly after the sulphur has been removed. The sodium sulphite solution must be heated very nearly to the boiling-point. The solution may be tested for sulphur by acidifying and allowing to stand for a few moments. A milky precipitate indicates sulphur. The removal of the sulphur by either of these solutions is incomplete.

On drying at 100° BISMUTH SULPHIDE first loses water and then begins to oxidize and gain in weight. This precipitate should therefore be weighed after drying for half an hour. The drying

for periods of half an hour and weighing is continued until the weight is constant or begins to increase. The lowest weight found is that of the dry sulphide.

75. The Sulphides of Tin cannot be weighed as such, but are converted into the *dioxide* by ignition in the air. The heat must be applied gently at first or some of the tin will be volatilized as sulphide. The stannic sulphide is more volatile than the stannous sulphide. When sulphur dioxide is no longer given off copiously the precipitate is heated more intensely. To completely expel the oxides of sulphur a little powdered ammonium carbonate is sprinkled over the precipitate, which is again ignited.

Antimony sulphide is ignited in the same manner and converted into the tetroxide Sb_2O_4 .

EXERCISE 20.

Determination of Copper in Copper Sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

Weigh out 1 gram of pure crystallized copper sulphate. Transfer to a 300-c.c. beaker and dissolve in about 200 c.c. of water. Add a few cubic centimeters of hydrochloric acid, heat nearly to boiling, and pass hydrogen sulphide until precipitation is complete. Allow the precipitate to settle for a few minutes, decant the solution through the filter, and transfer the precipitate. Wash with hydrogen-sulphide water. Before discarding any portion of the filtrate, test for copper with hydrogen sulphide. Copper sulphide is very readily oxidized by the oxygen of the air to copper sulphate, which passes through the filter-paper. The hydrogen sulphide of the wash-water is present to reprecipitate this dissolved copper. The precipitate should be exposed to the air as little as possible. For this purpose it should be washed down into the point of the funnel and kept well covered with the wash-water containing hydrogen sulphide.

76. Ignition of the Precipitate with Sulphur in a Stream of Hydrogen.—The precipitate is dried in the steam-oven, detached from the paper and placed in a weighed Rose crucible. The paper is then burned and the ash added to the precipitate. If the paper crumbles considerably, it may be placed in a porcelain dish or crucible and burned by heating the dish or crucible. Unburned particles of carbon sometimes remain unless the dish is heated strongly for some time. The residue is transferred to the crucible, the contents of which are mixed with an equal bulk of powdered sulphur which leaves no residue on ignition. A gentle stream of dry hydrogen is now led in through the porcelain tube which passes through the lid of the crucible. The hydrogen is freed from arsine by passing through a solution of mercuric chloride. The arrangement of the apparatus is shown in Fig. 12, page 63. The hydrogen must be allowed to pass until the air has been displaced from the wash-bottles as well as from the crucible.

About ten minutes is generally sufficient if the stream of hydrogen passes quite rapidly. The danger of explosion is greatly reduced if a plug of glass wool or cotton is loosely inserted in the glass tube nearest to the crucible. The crucible is at first heated gently with the Bunsen burner, and when the excess of sulphur is nearly all volatilized it is heated to redness with the full flame of the burner. After a few minutes' strong heating the burner is removed and the crucible is allowed to become very nearly cold in the stream of hydrogen. It is then placed in the desiccator and after a few minutes is weighed.

The precipitate is again mixed with sulphur, heated in the stream of hydrogen and weighed. This is repeated until constant weight is obtained. The percentage of copper in crystallized copper sulphate is 25.47. The ignited precipitate is cuprous sulphide, Cu_2S .

EXERCISE 21.

Determination of Arsenic in Arsenious Oxide, As_2O_3 .

Weigh out about 0.3 gram of pure resublimed arsenious oxide. Transfer to a small beaker and dissolve in a little freshly made dilute solution of caustic soda. Transfer the solution to a 250-c.c. Erlenmeyer flask. Acidify with hydrochloric acid and then add about 30 c.c. of the dilute acid. Dilute to about 200 c.c. or until the flask is nearly full and pass hydrogen sulphide until precipitation is complete. Filter immediately through a Gooch crucible which has been dried at 100° to constant weight. Wash with about 250 c.c. of water containing a few cubic centimeters of dilute hydrochloric acid* and a considerable amount of hydrogen sulphide. Suck the water out as completely as possible with the filter-pump, wash two or three times with alcohol, place the crucible in a small beaker and pour in carbon disulphide until the precipitate is covered. The carbon disulphide used for this purpose should leave no residue on evaporating a few cubic centimeters on a watch-crystal. If a residue is left, the carbon disulphide must be redistilled. Allow to stand about fifteen minutes. Pour off the carbon disulphide and extract again with a fresh portion. Continue this operation until a portion of the carbon disulphide evaporated on a watch-crystal leaves no deposit of sulphur. Dry the precipitate in the steam-oven and weigh. Theoretical percentage of arsenic in arsenious oxide is 75.75.

77. Precipitation of Zinc as Sulphide.—Zinc as well as manganese and iron are precipitated by ammonium sulphide in alkaline solution. Zinc may be precipitated by hydrogen sulphide in a solution which is only very slightly acid with a mineral acid or moderately acid with acetic acid. This sulphide is so finely divided that it passes through the filter-paper, making it very

* The acid prevents the formation of a "colloidal" solution

difficult to filter and weigh. If some *mercuric chloride* is added to the zinc solution, a precipitate is obtained which can be filtered and washed with ease. In the subsequent ignition the mercury is completely volatilized. The zinc sulphide obtained by adding ammonium sulphide to a solution of zinc made strongly alkaline with caustic soda is also easily washed, but it generally is contaminated with alkali and silica.

78. The Two Sulphides of Manganese.—Manganese forms two sulphides, one of which is green, while the other is pink. The pink sulphide resembles the sulphide of zinc in being so finely divided that filtration is difficult. The green sulphide on the other hand offers no difficulty of this kind in manipulation. It is, therefore, highly desirable to obtain this variety in determining manganese. This is accomplished by placing an excess of colorless ammonium sulphide together with some ammonium chloride in an Erlenmeyer flask, diluting to about 100 c.c. and heating nearly to boiling. The concentrated and hot manganese solution is then added all at once, and the flask vigorously shaken. The solution is kept hot and occasionally vigorously agitated, until the sulphide changes from pink to green and settles readily, leaving a clear supernatant liquid. Failure to obtain this result is generally due to the presence of an insufficient amount of ammonium sulphide. The precipitate is filtered immediately, and washed with water containing ammonium sulphide and ammonium chloride.

79. Precipitation of Iron as Sulphide.—Iron is precipitated as sulphide from solutions containing *organic matter*, which prevents the complete precipitation of the metal in the usual manner as hydroxide. Ammonium chloride must be present, and either the yellow or colorless ammonium sulphide may be used for precipitation. The solution must stand in a warm place until the precipitate has completely settled, leaving a clear supernatant fluid. Ammonium chloride and sulphide must be present in the wash-water, as the sulphide oxidizes to sulphate, which passes through the filter-paper unless it is reprecipitated by the ammonium sulphide. The bulk of the dried precipitate should be removed from the paper before burning the latter, though there is no danger of losing iron. The oxide formed during the com-

bustion of the paper is reconverted to sulphide by ignition in hydrogen after the addition of sulphur.

EXERCISE 22.

Determination of Manganese in Potassium Permanganate, KMnO_4 .

Weigh out one-half gram of pure potassium permanganate. Transfer to a small beaker, add a few cubic centimeters of conc. hydrochloric acid, cover with a watch-crystal, and evaporate to dryness on the water-bath. Dissolve in a few c.c. of water and neutralize the solution with ammonia.

Prepare some colorless ammonium sulphide by adding 100 c.c. of water to 50 c.c. concentrated ammonia (sp. gr. 0.90), saturating half of this solution with hydrogen sulphide and then adding the other half of the solution. In an Erlenmeyer flask of about 250 c.c. capacity is placed 25 c.c. of the ammonium sulphide solution, 10 c.c. of a five times normal solution of ammonium chloride or about 3 grams of the dry salt. The solution is diluted to about 100 c.c. and warmed on the hot plate or with a Bunsen burner. *As soon as it comes to a boil* the hot manganese solution is added, the beaker being rinsed with a little water. The flask is shaken vigorously and the solution kept nearly at the boiling-point. After alternate shaking and heating for a few minutes the manganese sulphide which came down pink turns green and settles readily, leaving a clear supernatant liquid. Failure to secure this result is due to the absence of a sufficient amount of ammonium sulphide, the reagent being weak or the salt was boiled away before adding the manganese solution. If the addition of more ammonium sulphide and heating fails to produce the green precipitate, the operation should be repeated, using more ammonium sulphide.

The green sulphide is allowed to settle for half an hour, the solution being kept warm. The precipitate is then filtered off and washed with water containing ammonium sulphide and ammonium chloride. It is dried and detached from the paper, which is burned, the ash being placed on top of the precipitate in a weighed porcelain crucible. The precipitate is mixed with two or three times its bulk of sulphur which is free from non-volatile matter. It is ignited in a stream of hydrogen which has been passed through a solution of mercuric chloride to free it from arsine and then dried over calcium chloride or concentrated sulphuric acid. The crucible is heated, at first gently, until the sulphur begins to burn, and then with the full flame of a Bunsen burner, giving a flame at least 15 cm. long when burning free. The crucible is allowed to become nearly cold in the stream of hydrogen. If brown particles of oxides of manganese are still visible, the precipitate should be again ignited after mixing with sulphur, and after cooling in the stream of hydrogen is transferred to the desiccator, completely cooled and weighed. No further change in weight should be observed on again heating with sulphur in the stream of hydrogen.

CHAPTER VII.

DETERMINATION OF METALS AS PHOSPHATE, ARSE-NATE, CHROMATE, AND CHLORIDE.

MANGANESE, ZINC, and MAGNESIUM may be precipitated and weighed as phosphates. Although most of the metals form phosphates which are quite insoluble, only those of the three metals mentioned are sufficiently insoluble or stable on ignition for quantitative determination. Phosphoric acid is one of the most non-volatile acids, but on account of its weak affinity and tendency to form acid salts it is difficult to procure a precipitate of constant composition. It may also be reduced more or less completely during the combustion of the filter-paper.

80. Precipitation of Manganese and Zinc.—With zinc and manganese an amorphous precipitate is first formed. This is the neutral metallic phosphate $M_3(PO_4)_2$,* and must be converted into the double ammonium phosphate MNH_4PO_4 . This is accomplished by heating the amorphous precipitate with the solution containing a large amount of ammonium chloride. 20 grams of the dry salt should be present for 0.2 gram of the metal. 5 to 10 c.c. of a cold saturated solution of microcosmic salt is then added and the solution diluted to 200 c.c. The solution is then cautiously neutralized with ammonia, and on the first appearance of a precipitate it is heated nearly to boiling and vigorously stirred until the amorphous phosphate has become crystalline. Ammonia is added drop by drop and the stirring continued after each addition of ammonia until the precipitate is crystalline. The addition of ammonia and the stirring is continued until no further precipitate forms. With manganese a large excess of ammonia should be avoided. The zinc solution should be made exactly neutral. The heating of the solution must be continued during the addition of ammonia until the phosphate is completely pre-

* In this formula M may be either Mn or Zn.

precipitated and converted into the crystalline form. A platinum dish is most suitable for this purpose. A porcelain dish is preferable to a beaker, as the latter is attacked by the hot alkaline solution, contaminating the precipitate with silica. The solution should contain no other metals than the alkalis. The precipitate is washed with water containing ammonium nitrate.

81. Magnesium forms a crystalline precipitate much more readily than zinc and manganese. The precipitation is carried out in a cold solution which must be allowed to stand for at least twelve hours in order to secure complete precipitation. If the solution is stirred or vigorously shaken, the precipitation is complete in an hour or two. If the amount of ammonium salts present is considerable, the magnesium is precipitated more slowly, requiring at least twenty-four hours' standing. In this case the composition of the precipitate is also different, containing relatively more ammonia. Such a precipitate is not suitable for weighing, but must be dissolved in the least amount of hydrochloric acid and reprecipitated by the addition of a little alkali-phosphate solution and ammonia drop by drop with vigorous stirring. The volume of the solution should be kept small on account of the solubility of the precipitate. It should not exceed 100 c.c.

82. Removal of Ammonium Salts.—If one does not wish to make two precipitations in this manner, the ammonium salts must first be removed. A very convenient method of accomplishing this object is that suggested by J. L. Smith. The solution is evaporated in a casserole or porcelain dish over the free flame to a sirupy consistency. Dilute nitric acid is then added in small portions, and the heating continued until nitrous fumes are no longer evolved. A little hydrochloric acid is then added in small portions and the heating continued until the excess of nitric acid is decomposed and chlorine is no longer evolved.

The ammonium salts may also be removed by evaporating the solution to dryness in a porcelain dish and gently heating the residue. The magnesium remains as oxide and is dissolved in hydrochloric acid. The solution is then made alkaline with ammonia. If a precipitate of magnesium hydroxide is formed, the solution should be acidified with hydrochloric acid and

again made alkaline with ammonia. This operation should be repeated until no precipitate occurs on making the solution alkaline. Finally the solution is acidified and a solution of disodium phosphate added in sufficient amount to precipitate all of the magnesium. It is then made alkaline by the addition of ammonia with constant stirring until no further precipitate is formed. The solution must be allowed to stand twelve hours before filtering off the precipitate. A few drops of the clear liquid should give a distinct test for phosphoric acid with magnesia mixture, otherwise enough of the precipitant has not been added. The precipitate is washed with dilute ammonia, one part of strong ammonia to ten parts of water.

83. Ignition of Phosphate Precipitates.—All of the phosphate precipitates lose ammonia and water on ignition and are converted into pyrophosphates according to the equation



If too much ammonium salts have been present in the solution, the precipitate will contain more ammonia than corresponds to the formula NH_4MPO_4 . Some metaphosphate of the metal, $\text{M}(\text{PO}_3)_2$, will be formed on the ignition of such a precipitate. The metaphosphate loses phosphorous pentoxide, and is converted into pyrophosphate only after very prolonged and intense ignition. Such a precipitate could be considered constant only when it does not lose weight after a half-hour's ignition with the blast-lamp. For this reason the excess of ammonium salts is removed before precipitation, as already directed. The evolution of ammonia and water is quite rapid if the precipitate is heated strongly, resulting in appreciable loss of material due to spattering. The precipitate should therefore at first be heated very gently with the Bunsen burner with the lid on the crucible. When no more ammonia is evolved the crucible may be heated with the blast-lamp.

As the phosphates fuse readily, the complete combustion of the filter-paper is secured with some difficulty. It is best to dry the precipitate and remove it as completely as possible from the paper, and burn the latter on the platinum wire, using the oxid-

izing flame of the Bunsen burner to assist the combustion. If the ash which falls into the crucible contains carbon which cannot be burned by simple ignition, it may be moistened with a drop or two of concentrated nitric acid which is volatilized by gentle heat and the ignition continued. The difficulty experienced in burning the carbon is frequently due to insufficient washing of the precipitate, so that it still contains sodium acid phosphate.

If the platinum crucible is used for the ignition of phosphates, it is sometimes damaged by the reduction of the phosphates and the union of the phosphorus with the platinum. The likelihood of damage seems to be much reduced if the moist precipitate and paper are introduced into the crucible and the ignition conducted by gradually bringing the crucible to redness with the Bunsen burner. The reducing gases from the flame must be absolutely excluded. Ignition of the precipitate in a porcelain crucible is entirely satisfactory.

EXERCISE 23.

Determination of Magnesium in Magnesium Sulphate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

Weigh out 1 gram of the pure recrystallized salt. Transfer to a small beaker and dissolve in 50 c.c. of water. Add 5 c.c. dilute hydrochloric acid and 15 c.c. of disodium phosphate solution. Add dilute filtered ammonia slowly with vigorous stirring, being careful to avoid rubbing the sides of the beaker with the stirring-rod, as very firmly adhering crystals would form where the beaker is rubbed. Add a few c.c. of ammonia in excess, allow it to stand for twelve hours, then transfer to a funnel containing a small paper and wash with dilute filtered ammonia (1 part of strong ammonia to 10 parts of water). The filtrate may be tested for chlorides by acidifying with nitric acid and adding a drop of silver nitrate solution. As the ammonia frequently contains chlorides, the washing should be continued until the filtrate gives no more turbidity with silver nitrate than the dilute ammonia.

The precipitate is dried in the steam-oven, removed from the paper quite completely by means of a brush and transferred to a watch-crystal. The paper is burned on the platinum wire, heating the charred portions from time to time in the oxidizing flame of the Bunsen burner. The ash is allowed to drop into a weighed porcelain crucible. If unburned carbon still remains, the open crucible should be placed on its side and heated with the Bunsen burner. If necessary, the combustion is completed by allowing the crucible to cool, adding a few drops of concentrated nitric

acid and placing the lid on the crucible and heating gently until the nitric acid is volatilized. When the carbon has been completely burned the main portion of the precipitate is added and the covered crucible very gently heated until no more ammonia fumes escape. It is then heated with the full flame of the Bunsen burner and finally for five or ten minutes with the blast-lamp. It is then weighed and again heated with the blast-lamp and weighed. This is repeated until constant weight is obtained. Theoretical percentage of magnesium in crystallized magnesium sulphate is 9.88.

84. Determination of Arsenic as Magnesium Pyroarsenate.—

When present in its higher state of oxidation arsenic may be precipitated as magnesium ammonium arsenate, which is ignited and weighed as magnesium pyroarsenate, $Mg_2As_2O_7$. Solution of compounds of arsenic in hydrochloric acid and potassium chlorate, aqua regia, or strong nitric acid converts the arsenic into arsenic acid.* The solution is filtered if necessary, evaporated to a small bulk, neutralized with ammonia, and magnesia mixture added with stirring. Alcohol is added to the extent of one-fourth of the volume of the solution. After standing twelve or, still better, as long as forty-eight hours the precipitate is filtered off and washed with a mixture of 2 volumes of strong ammonia, 2 volumes of water, and 1 volume of alcohol.

The precipitate is dried, detached from the paper and placed on a watch-crystal. The paper is returned to the funnel and the remaining portions of the precipitate dissolved in hot dilute nitric acid, and the paper washed with hot water. If it is not large, the entire precipitate may be dissolved in nitric acid. The solution is evaporated to dryness in a weighed porcelain crucible and the remainder of the precipitate added. With the lid on, the crucible is heated very gently until the ammonia is expelled. There is great danger of loss of arsenic before the ammonia is expelled because of its reducing action on the arsenic. The presence of nitric acid tends to prevent this, while by heating in a stream of oxygen the time required to expel the ammonia may be reduced to ten minutes. Moistening the precipitate with nitric acid is almost as efficient. When the ammonia is completely expelled the crucible is heated to redness with the Bunsen burner. The

* Note for student: Write the equations for these reactions.

precipitate is then magnesium pyroarsenate, $\text{Mg}_2\text{As}_2\text{O}_7$. The precipitate may also be collected on a Gooch crucible and ignited with the precautions given.

85. Determination of Lead, Barium, and Chromium as Chromates.—Lead and barium form very insoluble chromates which are of definite composition and may be completely dried without suffering decomposition. These precipitates may therefore serve to determine not only lead and barium, but also chromium. The precipitation is carried out in a solution acid with acetic acid. In determinations of lead and barium, potassium dichromate is used as the precipitant, while chromic acid is precipitated by lead acetate or barium chloride. Solutions acid with hydrochloric or nitric acid are rendered acid with acetic acid by addition of sodium acetate. The precipitate is washed with water, filtered on a Gooch crucible, and dried on the hot plate, or it may be gently ignited with the Bunsen burner, care being taken not to allow it to fuse.

86. Determination of Potassium as Platino-chloride.—Potassium may be precipitated as potassium platino-chloride, collected on a Gooch crucible which has been dried at 100° and weighed, or it may be collected on a filter-paper, washed with 80% alcohol, dissolved in hot water, and the solution evaporated to dryness on the water-bath in a dish and weighed. The precipitate may also be decomposed by ignition with a reducing agent, such as oxalic acid, or in a stream of hydrogen. The potassium then remains as chloride and is washed out of the reduced spongy platinum by hot water. The platinum may then be gently ignited and weighed. Potassium platino-chloride is soluble in 100 parts of cold water and 20 parts of hot water, in 40,000 parts of absolute alcohol and 25,000 parts of 80% alcohol. The presence of sodium platino-chloride and excess of the precipitant, platinum tetrachloride, or, more correctly, chlorplatinic acid, decreases the solubility. As the precipitate is washed with alcohol, salts insoluble in this liquid must be absent. Practically the solution may contain only chlorides of sodium and potassium but sufficient platino-chloride solution must be added to convert both of these salts into the double platinum salt.

87. Lindo-Gladding Method.—If the Lindo-Gladding method

of determining potassium is used, sulphates may be present, but the heavy metals should be absent. If chlorides are not present, sodium chloride should be added, and after the addition of an excess of platino-chloride solution the solution is evaporated to a sirupy consistency. The sodium platino-chloride and the excess of the precipitant is washed out by means of 80% alcohol. The sulphates are washed out with a solution of ammonium chloride made by dissolving 100 grams in 500 c.c. of water and shaking up the solution with 10 grams of potassium platino-chloride. The ammonium chloride is now washed out with 80% alcohol. While the Lindo-Gladding method has been extensively used by American chemists, the German workers still prefer to remove sulphates by precipitation with barium chloride.

88. Determination of Silver as Chloride.—Silver as well as mercury and bismuth may be precipitated as chloride and weighed as such. The neutral or slightly acid solution of silver is precipitated by the addition of hydrochloric acid or sodium chloride. It should be heated nearly to boiling before precipitation and the chloride added while stirring the solution vigorously. For this purpose it is convenient to place the solution in an Erlenmeyer flask. The addition of a considerable excess of chloride should be avoided, as silver chloride is appreciably soluble both in hydrochloric acid and in sodium chloride. After each addition of the reagent, and vigorous shaking or stirring of the solution, the precipitate should be allowed to settle and a drop of chloride added to the clear liquid. If a precipitate appears, more of the precipitant must be added. When the silver has been completely precipitated the solution should be heated on the hot plate or the water-bath with occasional stirring until the solution is clear. The precipitate is filtered off on a Gooch crucible which has been dried on the hot plate or in an air-bath at a temperature above 120°. Silver chloride loses chlorine when exposed to light, acquiring a blue color. It should therefore be protected as much as possible during the manipulation from the action of strong light.

It may also be filtered off on paper and washed, as already described. The precipitate is dried and removed from the paper as completely as possible and placed on a watch-crystal. The paper is now burned in a weighed porcelain crucible. The silver

chloride left on the paper is reduced to metallic silver. It is reconverted to chloride by the addition of a drop of nitric acid and one of hydrochloric and evaporating to dryness. As silver chloride is quite volatile, the amount left on the paper should be very small. The main portion of the precipitate is now transferred to the crucible and dried by gently heating with the Bunsen burner. The precipitate must not be allowed to fuse. The Bunsen burner, having a small flame, should be held in the hand, and immediately removed when the precipitate begins to fuse around the edge. The results are very accurate if the determination is properly carried out.

89. Washing the Precipitate without Filtration.—The silver chloride may also be washed and transferred to a crucible without

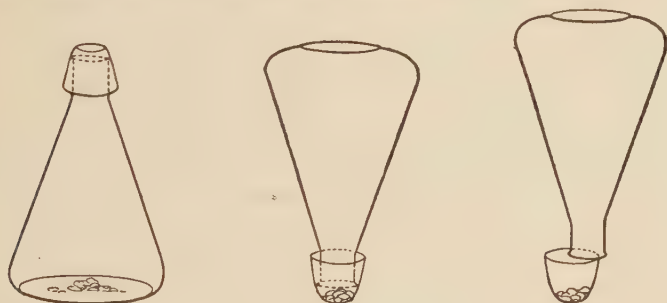


FIG. 14.

the use of filter-paper. The precipitation is carried out in an Erlenmeyer flask. When all of the silver has been precipitated the flask is shaken vigorously, until the liquid is perfectly clear and the precipitate has collected into a compact mass. The liquid is carefully decanted, and the precipitate washed by decantation. The flask is then filled with water, and a weighed porcelain crucible inverted over the mouth of the flask. By quickly inverting the flask the precipitate falls into the crucible, which is placed on the desk while the flask is held upright with the mouth in the bottom of the crucible. By gently tapping the flask any adhering particles of the precipitate fall into the crucible. By tilting the flask slightly, bubbles of air enter and the water flows quietly into the crucible. When the latter is full the flask may be removed by quickly passing it to one side of the crucible.

The water in the crucible is decanted as much as possible, the portion remaining being evaporated on the water-bath. The precipitate is then heated in the usual manner and weighed.

90. Determination of Mercury as Mercurous Chloride.—For precipitation as chloride, mercury must be in the mercurous condition. The cold and highly dilute solution is mixed with sodium chloride solution until precipitation is complete. After allowing the precipitate to settle, filter on a Gooch crucible dried at 100°. Wash with cold water. Weigh after drying at 100°. If the solution contains much nitric acid it should be nearly neutralized with sodium carbonate before precipitation of the mercury. If the metal is present in the solution as mercuric mercury, it may be reduced by means of phosphorous acid. Hydrochloric acid together with excess of phosphorous acid is added to the cold solution, which is allowed to stand for twelve hours cold or heated not higher than 60°. The precipitate of mercurous chloride is filtered off, washed, dried, and weighed as already directed.

91. Determination of Bismuth as Oxychloride.—Bismuth is precipitated and weighed as the oxychloride, BiOCl . If the solution is strongly acid, potassium, sodium, or ammonium hydroxides are added until not over $\frac{1}{2}$ per cent of free acid remains. If chlorides are not present, ammonium chloride is added and the solution is then largely diluted by the addition of water. After standing some time water is added to a portion of the clear liquid. If a precipitate forms, more water must be added to the entire solution. When all of the bismuth has been precipitated the oxychloride is filtered off on a Gooch crucible which has been dried at 100°. It is washed with water containing a few drops of hydrochloric acid, dried at 100°, and weighed. If sulphuric or phosphorous acids are present, small quantities of these acids are apt to contaminate the precipitate. The solution should contain only nitric and hydrochloric acids. Because of the tendency of the precipitate to lose chlorine, the results are not quite as reliable as when the bismuth is weighed as oxide. A little hydrochloric acid is added to the wash-water to prevent this loss.

EXERCISE 24.

Determination of Silver in Silver Nitrate, AgNO_3 .

Prepare a Gooch crucible with a layer of asbestos about $\frac{1}{2}$ cm. thick. Wash until no fine particles of asbestos come through with the wash-water. Dry on the hot plate or in an air-bath at 120° to 150° and weigh. Usually two hours' drying is sufficient.

Weigh out $\frac{1}{2}$ gram of silver nitrate and transfer to a 250-c.c. Erlenmeyer flask. Dissolve in 100 to 150 c.c. of water and heat nearly to boiling. Add dilute hydrochloric acid, a few drops at a time, shaking the flask vigorously after each addition. To avoid adding a large excess of the acid notice after each addition if a precipitate is produced. When sufficient hydrochloric acid has been added the flask should be warmed and vigorously shaken until the curdy precipitate is well collected and the solution is very nearly clear. Decant the clear liquid on the weighed Gooch crucible, wash two or three times by decantation, using hot water which contains a few drops of concentrated nitric acid. Finally transfer the precipitate to the crucible, using the "policeman" to clean the flask if necessary. Dry the Gooch crucible as before and weigh. The silver chloride should be exposed to the light as little as possible. The theoretical percentage of silver in silver nitrate is 63.50.

REVIEW.—At this point the student is advised to review the determinations of the metals by tabulating the methods as follows: In the first column write the name or symbol of each metal studied. In the next column headed "Precipitated as" write the formulas of the precipitates in which each element may be separated from solution. In the next column headed "Remarks, sources of error, etc.," indicate briefly the special precautions to be observed in each precipitation. In the next column headed "Weighed as" give the formulas of the dried or ignited precipitates. In the next column headed "Methods of drying" state whether the precipitate is dried at 100° on the hot-plate or by ignition.

DETERMINATION OF ACIDS.

CHAPTER VIII.

DETERMINATION OF THE HALOGENS, SULPHUR, AND NITROGEN.

THE gravimetric determination of acids is more difficult than the determination of metals because the acid radicals are as a rule more volatile and unstable than the metallic compounds. In the determination of metals various acid radicals have formed a part of precipitates which can be washed and weighed. Among these are the carbonates of the alkaline-earth metals; the sulphates of lead and barium, the sulphides of mercury, cadmium, silver, and arsenic, the phosphates of magnesium, zinc, and manganese, the chromates of barium and lead, and the chlorides of silver, mercury, and bismuth. In a good many cases it is found possible to use a given precipitate for the determination of either the metal or the acid radical.

DETERMINATION OF THE HALOGENS.

92. Precipitation as the Silver Salt.—Where a given acid forms a weighable precipitate with several metals, choice is made of the most insoluble and most stable precipitate. The CHLORIDE OF SILVER has been found to be the most advantageous form in which to precipitate and weigh either silver or the chlorine radical. In the determination of a chloride or of hydrochloric acid the process is very nearly identical with the determination of silver as given on page 90. The chloride solution must be slightly acid. For this purpose the neutral or alkaline solution is acidified with nitric acid, adding a drop or two in excess to the neutral solution. The solution is heated to about 60° and silver nitrate solution added with constant stirring until no more precipitate is formed. The solution is then heated nearly to boiling and stirred vigorously until the precipitate coagulates, leaving a clear superna-

tant liquid. Failure to secure this result may be due to the absence of an excess of silver nitrate. The precipitate is filtered off on a weighed Gooch crucible and washed with hot water containing a little silver nitrate. The presence of silver nitrate reduces very much the solubility of silver chloride in water. When the other impurities have been washed out the silver nitrate is removed by washing with as little distilled water as possible. The precipitate is then dried on the hot plate, or in an air-bath at about 150°. Silver chloride should be protected from the light as much as possible, as it turns dark, losing chlorine. The method gives very accurate results. IODIDES and BROMIDES as well as the free acids may be determined in the same manner.

93. Ignition of Paper.—If a Gooch crucible is not at hand, the silver halides may be filtered off on paper, washed in the manner already described, and dried. The precipitate is then separated from the paper as completely as possible and placed on a watch-crystal. The paper is burned on the platinum wire or in a weighed porcelain crucible. The SILVER CHLORIDE or BROMIDE remaining on the paper is reduced to metallic silver. The ash of the paper in the crucible is treated with a drop or two of nitric acid and a drop of hydrochloric or hydrobromic acid to reconvert the silver into the proper halide salt. The excess of acid is evaporated off by gentle heat and the remainder of the precipitate added. The crucible is now heated very gently with the Bunsen burner, care being taken not to fuse the precipitate, which volatilizes slightly when fused. The SILVER IODIDE which remains on the filter-paper is not reduced when the latter is burned, but on account of its volatility it should be removed as completely as possible. The silver precipitate may also be washed without filtration as described in Chapter VII, page 91.

94. Determination of the Halogens in Metallic Salts.—The chlorine in MERCURIC CHLORIDE, STANNOUS CHLORIDE, PLATINIC CHLORIDE, the CHLORIDE of ANTIMONY, and the GREEN CHLORIDE of CHROMIUM cannot be determined by precipitation with silver nitrate. The precipitate is contaminated in the case of the stannous salt with stannic oxide and silver oxide, in the case of the mercuric and antimony salts with metallic mercury or antimony. All of the chlorine is not precipitated from the chromium solution.

Platinous chloride contaminates the precipitate of silver chloride from platinic chloride. The tin in stannous chloride is therefore precipitated by boiling the concentrated neutral solution with ammonium nitrate. The mercury and antimony are precipitated with hydrogen sulphide, tartaric acid having been added to the antimony solution. The chlorine in platinic chloride may be determined by fusing the salt with sodium carbonate, filtering off the platinum from the solution of the fusion and determining the chlorine in the filtrate. The chromium in the green chloride is precipitated by means of ammonia, filtered off and washed, and the chlorine precipitated with silver nitrate in the filtrate. The corresponding salts of BROMINE and IODINE are treated in a similar manner.

The INSOLUBLE CHLORIDES, of LEAD, SILVER, and MERCURY must be decomposed by alkalis for the separation of the metal. Silver chloride may be fused in a porcelain crucible with sodium and potassium carbonates. Lead chloride may be treated in the same manner or digested with alkali bicarbonates and water, while mercurous chloride may be decomposed by digestion with a solution of sodium or potassium hydroxide. The INSOLUBLE BROMIDES and IODIDES may be treated in a similar manner.

SEPARATION OF CHLORINE, BROMINE, AND IODINE.

95. Separation of Iodine as Palladous Iodide from Chlorine and Bromine.—Very excellent methods have recently been worked out for the separation of chlorine, bromine, and iodine. Iodine may be precipitated either as palladous or thallous iodide from solutions which contain chlorine or bromine. For the precipitation as palladous iodide the solution is made slightly acid with nitric acid and palladous nitrate added in slight excess. The solution is allowed to stand for twenty-four to forty-eight hours. The brownish-black precipitate of palladous iodide, PdI_2 , is filtered off on a Gooch crucible or on a tared paper, washed with warm water, and dried at 100° to constant weight. The paper may also be burned, and the precipitate ignited in a Rose crucible in a stream of hydrogen. It is then reduced to metallic palladium, and may be weighed as such.

If only hydrobromic or hydrochloric acid is present in the filtrate, it may be precipitated with silver nitrate, after removal of the excess of palladium with hydrogen sulphide. The excess

of hydrogen sulphide must be removed by means of ferric sulphate or hydrogen peroxide, and the precipitated sulphur filtered off after digesting some time on the water-bath. If sufficient material is at hand, the iodine may be determined by means of palladous nitrate or chloride in one portion, and the iodide together with the chloride or bromide precipitated and weighed as the silver salt in another equal portion. The weight of silver iodide is then calculated from the weight of the palladium precipitate and subtracted from the weight of the combined silver precipitate.

96. Separation of Iodine from Chlorine as Thallous Iodide.—

Iodine may also be separated from chlorine by precipitation as thallous iodide, according to Jannasch and Aschoff. Both thallous iodide and chloride are slightly soluble in cold water, the iodide less than the chloride, however. The presence of ammonium sulphate increases the solubility of the chloride and decreases the solubility of the iodide, which is almost absolutely insoluble if alcohol is present. To the solution of the chloride and iodide, which should have a volume of about 50 c.c., the same volume of 20% ammonium sulphate solution is added and 30 c.c. of alcohol. A 4% solution of thallous sulphate is now added until the iodide is precipitated. The solution is gently warmed, well stirred, and allowed to stand for twelve hours. The precipitate of thallous iodide, TlI , is filtered off on a Gooch crucible, and washed with a mixture of 5 parts ammonium sulphate, 70 parts of water, and 30 parts of alcohol. It is dried at 100° . After expelling the alcohol from the filtrate the chlorine may be precipitated with silver nitrate after diluting considerably to prevent the precipitation of silver sulphate. For the same reason the solution should be digested hot for some time.

97. Separation of Chlorine, Bromine, and Iodine.—Jannasch and Aschoff have also worked out a method of separating the three halogens which depends on the fact that iodine is liberated from hydriodic acid by *nitrous acid*, while neither hydrochloric nor hydrobromic acid is oxidized under these conditions. The liberated iodine may be removed from the solution by means of carbon disulphide, or it may be volatilized with steam after diluting the solution so that neither hydrobromic nor hydrochloric

acid is expelled. *Ferric sulphate* and a number of other reagents have been found to liberate iodine and not chlorine or bromine. The hydrobromic acid may be oxidized by *potassium permanganate* and *acetic acid*, and the bromine driven out of the solution by means of steam. The chlorine may then be precipitated with silver nitrate.

A suitable arrangement of apparatus is shown in Fig. 15. The ground-glass joint of the tubes entering the flask *K* is very essen-

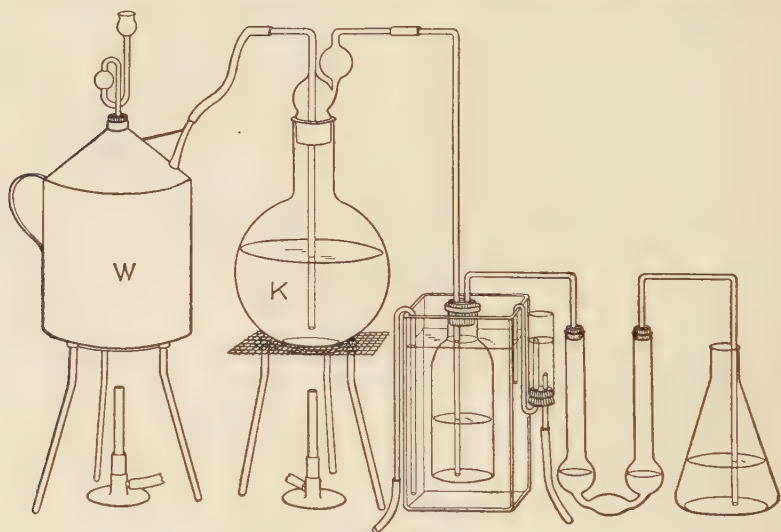


FIG. 15.

tial, as neither cork nor rubber is unacted on by the halogens. The most satisfactory substitute for a ground-glass joint is a cork stopper coated with paraffine. The stoppers in the absorption-flask as well as the Peligot tube are of this character. The distilling-flask *K* should have a capacity of at least 1 liter, and the absorption-flask a capacity of 500 c.c. *W* is a tin or metallic vessel for generating steam.

The neutral solution of the halogens is placed in the flask *K*, diluted to about 750 c.c. with water, 5 c.c. of dilute sulphuric acid added, as well as 1 gram of sodium nitrite dissolved in a little water. The flask is closed immediately. The absorption-flask should contain a mixture of 50 c.c. of caustic soda * solution and

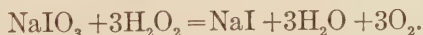
* If caustic soda free from the halogens is not at hand, it may be made by dissolving metallic sodium in distilled water.

an equal volume of hydrogen peroxide solution. The bulbs of the Peligot tube should be nearly filled with a similar solution, and a little dilute caustic soda solution should be placed in the Erlenmeyer flask.

98. Distillation of the Iodine.—On heating the contents of the flask *K* to boiling and passing a current of steam, the iodine is driven over into the absorption-flask, which is kept cold by means of the cold water in the beaker. The distillation is continued until the solution in *K* is colorless, which requires about fifteen minutes. All of the iodine will then be driven out. On being absorbed by the caustic soda, part of the iodine is converted into iodate according to the equation



The hydrogen peroxide present converts the iodate into iodide:



99. Determination of the Iodine as Silver Iodide.—While the steam is still passing, the delivery-tube is withdrawn from the absorption-flask and rinsed with a little water. The contents of the flask as well as the Peligot tube are transferred to a porcelain dish, 50 c.c. of hydrogen peroxide added, and the solution warmed for some time on the water-bath. Silver nitrate is added until a permanent precipitate of silver hydroxide is formed. On digesting the precipitate the brown silver hydroxide is converted into the yellow iodide. If the brown color disappears entirely, more silver nitrate must be added. Finally the solution is acidified with nitric acid, warmed, and the silver iodide filtered off on a Gooch crucible, washed with hot water, dried on the hot plate or in the air-oven at 150° and weighed.

100. Distillation of the Bromine.—The contents of the distilling flask are made faintly alkaline with caustic soda and concentrated to a volume of 500 c.c. The solution is cooled, 60 c.c. of 33% acetic acid is added, and 1 to $1\frac{1}{2}$ grams of potassium permanganate dissolved in a little water. The absorption flask and Peligot tube are filled, and the distillation conducted exactly as directed for the iodine. The bromine is expelled from the solution with more difficulty than in the case of the iodine, 45 to 75 minutes

being generally required. The distillation must be continued for some time after bromine vapors are no longer visible.

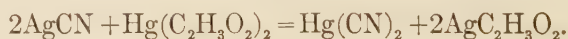
The solution of the bromine is transferred to a porcelain dish, 50 c.c. of hydrogen peroxide solution added, and warmed on the water-bath. The bromine is then precipitated, washed, and weighed in the same manner as the iodine.

101. Determination of the Chlorine.—The potassium permanganate in the distilling-flask is decomposed by neutralizing the solution with caustic soda, adding a little methyl alcohol and warming. The manganese dioxide is filtered off and washed with warm water. The chlorine in the filtrate is precipitated in the usual manner.

102. Determination of Chloric Acid.—Chloric acid may be determined by precipitation with silver nitrate after reduction with pure zinc and sulphuric acid.

103. Determination of Hydrocyanic Acid.—Hydrocyanic acid may be precipitated and weighed as silver cyanide. The solution should be dilute and slightly acid with nitric acid. Excess of silver nitrate is added to the cold solution with vigorous stirring. The precipitate may be collected on a weighed filter-paper or, still better, on a Gooch crucible and dried at 100°. It may also be collected on an unweighed filter-paper and converted into metallic silver by simple ignition until the weight is constant. This operation should be carried out in a porcelain crucible. Heating to redness for one-quarter hour is generally sufficient to completely decompose the cyanide.

104. Separation of Hydrocyanic Acid from Chlorides, Bromides, and Iodides.—If chlorides, bromides, or iodides are present in the solution of the cyanide, the precipitated silver salt of the halogen must be separated from the silver cyanide. For this purpose the precipitate is digested with a solution of mercuric oxide in dilute acetic acid. The silver cyanide is converted into soluble mercuric cyanide and silver acetate:



A solution of mercuric oxide in 100 c.c. of water and 5 c.c. dilute acetic acid is sufficient to dissolve the silver cyanide from 0.1 gram of potassium cyanide. The halogen salts of silver are not decom-

posed by the mercury solution, which is filtered off and the dissolved silver precipitated as chloride after the addition of nitric acid. The silver chloride must be ignited in a stream of hydrogen in a porcelain crucible. Some mercury is carried down with the silver and cannot be entirely removed by drying the silver chloride. The presence of the halogens do not interfere in the volumetric determination of cyanogen.

DETERMINATION OF SULPHUR.

105. Determination of Sulphur by Fusion with Alkali Carbonates and Nitrates.—Sulphur in sulphides and in most of its compounds is usually converted into sulphuric acid and precipitated and weighed as barium sulphate. Many methods of oxidation have been proposed for converting the various sulphur compounds into sulphuric acid or soluble sulphates. Perhaps the most generally applicable method is fusion with sodium carbonate and potassium nitrate. The finely powdered and weighed material is intimately mixed with six parts of dry sodium carbonate and four parts of potassium nitrate. The proportion of potassium nitrate should be reduced if the percentage of sulphur is small, as when much nitrate is present the action on the platinum crucible is considerable. This mixture is transferred to the crucible, and gradually heated until fused. The illuminating-gas used for the Bunsen burner frequently contains sulphur, which may be absorbed by the fusion mixture. To prevent this it is advisable to place the crucible in a hole cut in a piece of asbestos board.* The crucible should not be heated higher than necessary to keep the contents fused. When cool, dissolve the residue in hot water, filter, and wash with water containing a little sodium carbonate. Acidify the filtrate with hydrochloric acid and evaporate to dryness in a porcelain dish. Add a little dilute hydrochloric acid and evaporate to dryness again to completely remove the nitric acid. Dissolve the chlorides in water and a drop or two of dilute hydrochloric acid. Filter and wash the paper free from chlorides. The filtrate should have a bulk of about 250 c.c. Heat to boiling, add barium chloride solution slowly with constant stirring, digest

* As alcohol is free from sulphur the crucible is frequently heated with a spirit lamp.

hot until the solution is clear; filter, wash free from chlorides, ignite and weigh.

This method has been largely used for determining sulphur in sulphides, either minerals or laboratory products. If the sulphides lose sulphur on heating, the fusion mixture should consist of 4 parts of sodium carbonate, 8 parts of potassium nitrate, and 24 parts of pure and perfectly dry sodium chloride. As the reagents used may contain sulphur, a blank determination is necessary in careful work. For this purpose the fusion and precipitation must be carried out exactly as in the actual determination. The amount of barium sulphate obtained in this manner is deducted from that obtained in the analysis of the unknown.

106. Fusion of Sulphur Compounds with Sodium Peroxide.—Sulphur may also be oxidized to sulphuric acid by fusion with sodium peroxide. The finely ground material is mixed with five or six times its weight of powdered sodium peroxide, and the mixture fused in a nickel or copper crucible. The crucible must be covered with a closely fitting lid, and must be very cautiously heated, as the action is quite violent in the beginning. The flame of the Bunsen burner must be small and not touching the crucible. After a few minutes the heat is increased just sufficiently to keep the contents of the crucible in the state of fusion, which is maintained for a few minutes. The crucible is then allowed to cool, placed on its side in a beaker, and water added from a wash-bottle while a watch-crystal is held over the beaker. When the fused mass is dissolved the crucible and lid are taken out with a clean pair of tongs and washed with water. The solution is filtered, and the residue washed with water containing a little sodium carbonate. If the residue is small, and especially if it is free from iron, this filtration may be omitted. The filtrate is acidified with hydrochloric acid, and if silica was present in the original material the solution is evaporated to dryness finally on the water-bath, where it is heated for half an hour. The residue is treated with water and a few drops of hydrochloric acid and filtered. The sulphuric acid in the filtrate is precipitated and weighed as barium sulphate. As the sodium peroxide is not always free from sulphur, a blank determination must be made as in the preceding method.

107. Oxidation of Sulphur Compounds with Fuming Nitric Acid.—Digestion with red fuming nitric acid is one of the best of

the methods in which a liquid oxidizing substance is used. Most sulphides and sulphur compounds may be oxidized in an Erlenmeyer flask in the neck of which a small funnel is placed to prevent the too rapid escape of the fumes. With substances which are readily decomposed, giving off sulphuretted hydrogen, it is advisable to conduct the operation in a glass-stoppered bottle. A small, flat-bottomed glass tube or weighing-bottle, which may easily be inserted into the bottle, is provided. The material to be analyzed is weighed out and placed in this small tube, which is then lowered into the bottle so as not to spill the contents. The fuming nitric acid is now added from a graduate. 30 c.c. is sufficient for quantities of material which will yield not more than 1 gram of barium sulphate. The stopper is then inserted in the bottle and held firmly with the hand, while the bottle is tilted so that the acid comes in contact with the sulphide. When the first violent reaction has ceased shake the bottle a little, cool the bottle and contents by holding it under a tap of running water for a few minutes, and then cautiously remove the stopper so as to relieve the pressure without loss of material by spattering. The stopper is replaced in a slanting position to allow exit for the fumes, and the bottle is placed on the water-bath. If after half an hour's digestion particles of sulphur remain floating on the liquid, strong hydrochloric acid, potassium chlorate, or liquid bromine may be added in small portions, the potassium chlorate and liquid bromine being the most efficient. Care should be taken to prevent the fuming nitric acid or bromine from coming in contact with the hands, as serious burns are very quickly produced. The digestion on the water-bath is then continued until the sulphur is oxidized.

108. Decomposition of Insoluble Sulphates.—The complete disintegration of the material is frequently indicated by a change in color or physical appearance. The nitrates of the metals are generally insoluble in the concentrated acid. Insoluble sulphates, of such metals as barium and lead, may also be produced. In the case of minerals, gangue, quartz, etc., will be left. The concentrated acid is diluted with water and digested for a few minutes to dissolve soluble salts. If BARIUM is present, the insoluble material must be filtered off, washed thoroughly, and fused with five parts of mixed sodium and potassium carbonates. The melt is dis-

solved in water, and the insoluble carbonates filtered off and thoroughly washed. The filtrate is acidified with hydrochloric acid and added to the nitric acid solution. If LEAD is present, the sulphate of this metal may be decomposed by digesting with a solution of acid sodium or potassium carbonate, filtering, washing, and treating the filtrate as before.

109. Removal of the Nitric Acid.—The nitric acid solution, now containing all of the sulphur as sulphuric acid, is evaporated to dryness after the addition of a little sodium chloride, if alkalis have not already been introduced. The evaporation is repeated after the addition of dilute hydrochloric acid, until the nitric acid is entirely removed. The residue is dissolved in water, a few drops of hydrochloric acid are added, the solution is filtered if necessary, and the sulphuric acid determined as barium sulphate.

110. Other Oxidizing Solutions Used for Sulphur Compounds.—The digestion with LIQUID BROMINE or AQUA REGIA made by mixing one part of strong hydrochloric acid with three parts of strong nitric acid is carried out in a similar manner. The bromine may either be added gradually to the material mixed with a little nitric acid or to the dry material. These methods are largely used for the determination of sulphur in pyrites or crude sulphur. (See Exercise 36, p. 172.) The dry material may also be mixed with powdered POTASSIUM CHLORATE in an Erlenmeyer flask, and concentrated hydrochloric acid added in small portions. Finally the flask is gently heated on the water-bath. The subsequent treatment is identical with that given after treatment with nitric acid. A very powerful oxidizing agent consists of a saturated solution of potassium chlorate in concentrated nitric acid.

111. Oxidation of Sulphur Compounds by Means of Chlorine.—If lead is present, the oxidation of the sulphur by means of chlorine in alkaline solution is advantageous, because the lead is precipitated as peroxide. Iron is also precipitated as ferric hydroxide. On passing the chlorine for a considerable time, however, the iron passes into solution as ferrate, producing a red tint. Heating the liquid for a few minutes with powdered quartz serves to precipitate the iron. The finely powdered SULPHIDE or CRUDE SULPHUR is heated for some time with a dilute solution of caustic potash which is free from sulphuric acid. Free sulphur as well as

the sulphides of arsenic and antimony dissolve in the caustic potash. Chlorine-gas is now led into the warm solution for some time. Most of the metals together with the gangue remain in the precipitate, which is filtered off and well washed. The filtrate is acidified with hydrochloric acid, again filtered if necessary to remove silica, and the sulphuric acid determined as barium sulphate in the usual manner.

112. Determination of Tellurium and Selenium.—These elements are precipitated from acid solutions by means of sulphur dioxide or sodium or potassium sulphite. If the solution contains nitric acid it must be evaporated to dryness after the addition of hydrochloric acid and sodium or potassium chloride. The solution should be heated nearly to boiling, and kept at this temperature for a considerable time to insure complete precipitation. If the solution is dilute or a small amount of the element is present, it must be allowed to stand for several days in a warm place. The precipitate is washed by decantation with water containing sulphur dioxide, and finally transferred to a weighed filter-paper, or to a Gooch crucible, and dried at 100°.

DETERMINATION OF NITROGEN.

Nitrogen unites with hydrogen to form a fairly strong base, and with oxygen and hydrogen to form one of the strongest acids. The methods used for determining the nitrogen when it exists in one of these forms are not generally applicable to the determination of nitrogen in the other form. The methods most commonly used are volumetric. In this chapter the gravimetric methods, which are at times convenient, will be given.

113. Determination of Ammonia as Ammonium Chloride.—Ammonia may be weighed as ammonium chloride, which can be dried at 100°. A solution which contains nothing but free ammonia, ammonium chloride, or the ammonium salt of a very readily volatilized acid, such as carbonic acid or hydrogen sulphide, may be acidified with pure hydrochloric acid and evaporated to dryness on the water-bath in a weighed platinum dish. Many impurities, such as silica and the alkaline earth metals and the alkalis, do not interfere, since after weighing the residue in the dish the ammonium chloride may be volatilized by gentle heat, and the non-volatile residue weighed. Carried out in this manner the deter-

mination of ammonia is quickly and accurately made. It is a convenient method when so few determinations are required that the preparation of volumetric solutions is not warranted.

114. Determination of Ammonia as Ammonium Platino-chloride.—Ammonia may also be precipitated as ammonium platino-chloride which is washed with alcohol and dried at 100°, as described for potassium. The precipitate may also be decomposed by ignition into metallic platinum. The heat must be applied cautiously to the covered crucible, otherwise the escaping ammonium chloride will carry away platinum.

115. Determination of Nitric Acid by Means of Nitron.—No inorganic compound of nitric acid is known which is sufficiently insoluble to be used for the quantitative determination of this acid. Recently an organic base has been made which forms an insoluble nitrate.* This base is 1.4 diphenyl-3.5 endanilodihydrotriazol, having the formula $C_{20}H_{16}N_4$. For convenience in ordinary use and because it precipitates nitric acid, the name "nitron" has been given to the base. For use as a reagent a 10 per cent solution in 5 per cent acetic acid is made.

At ordinary temperatures nitron precipitates nitric acid from solutions of 1 in 60,000, while at 0° C it will precipitate 1 part in 80,000. Unfortunately nitron also precipitates a number of other common acids, such as hydrobromic when present to the amount of 1 part in 800 of the solution, hydriodic acid (1 in 20,000), chromic acid (1 in 6000), chloric acid (1 in 4000), perchloric acid (1 in 50,000), sulphocyanic acid (1 in 15,000), and nitrous acid (1 in 4000). These acids must therefore be first removed from the solution. Hydrobromic and hydriodic acids may be removed by adding chlorine water and boiling out the liberated halogen, or in the case of hydriodic acid it may be oxidized to the iodate. These acids may also be removed by means of silver sulphate. Nitrous and chromic acids may be reduced by means of hydrazine sulphate. To remove the nitrous acid the neutral concentrated solution (5-6 c.c.) is dropped slowly on one-fourth gram of finely powdered hydrazine sulphate. It is advisable to place the hydrazine sulphate in a small flask in order to avoid loss by spattering

* M. Busch Ber., 38, 861 (1905). J. Chem. Soc., 88, II, 282, 418 (1905).

and to facilitate cooling the mixture by means of cold water, as a small amount of nitric acid is formed if the mixture is allowed to become warm.

The volume of the solution of the nitrate or nitric acid should be small because of the slight solubility of the precipitate. About 0.1 gram of nitric acid should be present in a volume of 80 to 100 c.c. which has been acidified with 10 drops of sulphuric acid. The solution is brought almost to the boiling-point and 10 to 12 c.c. of the nitron reagent is added. The hot solution gives a crystalline precipitate. The beaker is then immersed in ice-water, where it is allowed to stand for one and one-half to two hours. The precipitate is filtered off on a Gooch crucible which has been dried at 110° . It is transferred to the crucible by means of the mother-liquor and is washed with small portions of ice-water, using not more than 10 to 12 c.c., the precipitate being sucked dry after each addition of ice-water. The precipitate is then dried at 110° until constant, which requires about three-fourths of an hour. The precipitate has the formula $C_{20}H_{16}N_4.HNO_3$, and contains 16.8% HNO_3 or 14.4% N_2O_5 .

116. Volatilization of N_2O_5 by Fusion of Nitrates with Silica or Potassium Chromate.—Some very excellent methods of determining nitric acid depend on its conversion into ammonia, nitric oxide, or nitrogen. Most of these methods will be described in the chapters on volumetric and gas analysis. It may also be determined indirectly by heating the dry nitrate with a weighed amount of silica or potassium-acid chromate until all of the nitric acid is expelled. The loss in weight is due to expulsion of N_2O_5 . The method can obviously not be applied to material which may lose anything but nitric acid. It has been extensively applied to sodium and potassium nitrates which can be dried at 130° and 100° respectively. The silica used must be finely powdered and ignited before being weighed. About seven times as much silica as nitrate must be taken. The material is intimately mixed and heated to redness in a platinum crucible for two to four hours or until constant weight is obtained.

Instead of the silica a mixture of equal parts of neutral and acid potassium chromate may be used. This material is fused in a platinum crucible, allowed to cool, and finely powdered. About 3 grams

of the chromate mixture are weighed out and placed in a platinum crucible. .8000 gram of the dried nitrate is added and thoroughly mixed with the chromate by means of a platinum or glass rod. The crucible is heated gently so as to gradually bring the contents to a state of fusion. When no more acid fumes are evolved, the crucible is cooled in the desiccator and weighed. It is reheated until constant weight is obtained.

CHAPTER IX.

DETERMINATION OF CARBONIC, BORIC, AND PHOSPHORIC ACIDS.

DETERMINATION OF CARBON DIOXIDE BY LOSS.

Two general methods are in use for the determination of carbon dioxide. By the first method the carbonate is decomposed by means of a strong mineral acid or other means, and the carbon dioxide expelled. The amount present is ascertained by weighing the apparatus before and after the expulsion of the carbon dioxide. By the second method the gas evolved by the decomposition of the carbonate is led into a caustic-potash solution, which is weighed before and after the absorption of the carbon dioxide. The gain in weight represents the amount of carbon dioxide present.

Various forms of apparatus have been devised for the determination of carbon dioxide by loss when the carbonate is decomposed by means of acid. Two of these will be described, one of which may be purchased complete, while the other may be put together from the usual laboratory apparatus.

117. The Schrötter Apparatus shown in Fig. 16 may be purchased ready for use. A weighed amount of the carbonate is placed in the small bulb *e* and the stopper *a* firmly inserted. The tube *c* is filled with dilute nitric or 10% hydrochloric acid, and *b* is about half filled with concentrated sulphuric acid. The entire apparatus is then carefully weighed. By opening the stop-cock *d*, acid is allowed to flow into *e* at such a rate that the bubbles of gas can readily be counted while passing through the concentrated sulphuric

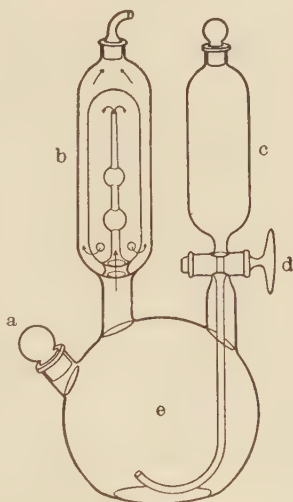


FIG. 16.

acid in *b*. When all of the acid has been allowed to flow out of *c*, and carbon dioxide is no longer evolved, the stop-cock *d* is closed and the solution in *e* is gently warmed on the water-bath or a hot plate to expel the carbon dioxide. The stop-cock *d* is now opened and air is sucked through the apparatus at a moderate rate until the carbon dioxide has been displaced. After being allowed to come to the atmospheric temperature, the apparatus is again weighed. The loss in weight represents the amount of carbon dioxide evolved.

118. Sources of Error in the Determination of Carbon Dioxide by the Schrötter Apparatus.—Though the manipulation of this apparatus is very simple, it is impossible to obtain results accurate within more than $\frac{1}{2}\%$. The error involved in weighing a glass apparatus of large surface is considerable. The gas which leaves the apparatus is dried over concentrated sulphuric acid, while that which enters is not dry. It is customary to ascertain when all of the carbon dioxide has been displaced by air by the taste of the gas which is sucked through by the mouth. The ordinary chemical tests for carbon dioxide cannot be used unless the air drawn through is freed from this gas. The accuracy of the method would undoubtedly be increased if the air drawn through were first passed through tubes containing soda-lime and concentrated sulphuric acid. Care must also be taken to have the apparatus at the same temperature each time it is weighed.

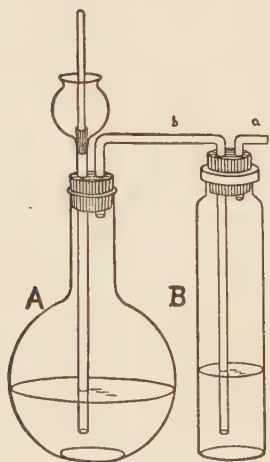


FIG. 17.

119. Simple Laboratory Apparatus for Determining Carbon Dioxide.—Various forms of apparatus which can be made from the usual laboratory material have been suggested. A very simple device is shown in Fig. 17. The small flask *A* is closed with a two-holed rubber stopper, through which the thistle-tube passes as well as the bent-glass tube *b*, the latter also passing to the bottom of the short test-tube or small bottle *B*. The thistle-tube is closed with a glass rod, over the end of which a short piece of rubber tube has been

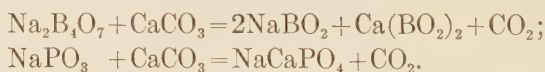
slipped. The weighed amount of the carbonate is placed in the flask, and covered with a little water. The rubber stopper is firmly inserted, and a few cubic centimeters of dilute hydrochloric acid placed in the thistle-tube. If the carbonate is completely decomposed by sulphuric acid, it may be used instead of the dilute nitric or 10% hydrochloric acid. The tube *B* is half filled with concentrated sulphuric acid. The apparatus is tested for gas leaks by drawing out a little air from the bottle *A*, by applying suction to the tube *a*. The sulphuric acid rises in the tube *b*, and should remain at the same height for several minutes. The apparatus is now carefully weighed, and the carbonate decomposed by allowing the acid in the thistle-tube to flow into the flask in small portions. When all of the acid has been introduced, the flask *A* is gently warmed to expel the carbon dioxide. The carbon dioxide is displaced with air by applying suction at *a*. In careful work the air must be purified before entering the apparatus by passing through soda-lime and concentrated sulphuric acid, these absorption-tubes being connected to the thistle-tube by means of a one-holed rubber stopper.

120. Determination of Carbon Dioxide by Fusion of Carbonates with Anhydrous Borax or Microcosmic Salt.—The carbon dioxide in all anhydrous carbonates may be determined by fusion with anhydrous borax. The carbon dioxide is completely expelled and its amount computed from the loss in weight. About 4 grams of vitrified borax are taken for 1 gram of the carbonate. The borax is placed in a platinum crucible, and heated with the Bunsen burner until the material is fused. It is allowed to cool in the desiccator and then weighed. As there is danger of loss by the cracking of the borax if cooled suddenly, the flame of the Bunsen burner is turned down gradually before placing the crucible in the desiccator. As the borax retains water somewhat persistently, it is advisable to fuse and weigh it again. The anhydrous material may be kept in a state of fusion for one-quarter to one-half hour without loss in weight. *The borax will be volatilized if heated with the blast-lamp.* The weighed quantity of the dry carbonate is placed on top of the borax, and the latter again fused. As there is danger of loss by the cracking of the borax on being heated, the crucible should be covered until the borax is melted. It must be kept melted until the carbonate

is dissolved and no more bubbles escape. A few generally remain in the fused mass, and cannot be expelled except by very prolonged heating. After being again cooled in the desiccator, the crucible is weighed. The loss in weight is due to carbon dioxide. The borax glass may generally be removed by pressing the crucible between the thumb and fingers, thus loosening the fused mass, which will drop out on gently tapping the inverted crucible.

Microcosmic salt may be substituted for borax in this determination.* This salt melts very easily, needing only a small flame of the Bunsen burner. The heating is continued until all of the ammonia and water has been expelled. It is cooled and weighed and reheated until the weight is constant. The weighed carbonate is then added and the contents of the crucible heated very cautiously to avoid loss by the foaming caused by the escape of carbon dioxide. When no more carbon dioxide escapes, the crucible is cooled and weighed. It is again heated until the weight is constant.

The action of the borax on the carbonate produces metaborates from the pyroborate, while the fused microcosmic salt is changed from the metaphosphate to the normal phosphate, according to the following equations:



DIRECT WEIGHING OF CARBON DIOXIDE.

The most reliable and accurate method of determining carbon dioxide is that in which the gas is absorbed and weighed. The carbonate is decomposed by sulphuric or hydrochloric acid. The gas evolved is dried, freed from hydrochloric acid, and absorbed in soda-lime or caustic-potash solution. The last portions of carbon dioxide are swept out of the apparatus by means of a stream of air which has been freed from carbon dioxide.

121. Apparatus.—Many forms of apparatus have been proposed and used for this purpose. The simplest and most serviceable form is that given by FRESSENIUS. The characteristic part of this apparatus consists of a long glass tube which acts as a condenser, and also holds the drying and purifying material. In other forms

* O. Lutz and A. Tschischikow, Jour. russ. phys.-chem. Gesellsch., 36, 1274.

of apparatus the drying materials are placed in a series of U-tubes which are connected by rubber tubing, stoppers, etc. The difficulties in making absolutely gas-tight joints are numerous, especially when the permeability of rubber to carbon dioxide is considered. The small number of joints in the apparatus of Fresenius gives it a decided advantage over other forms. In all forms of apparatus the carbonate is placed in a small flask closed with a two-holed stopper. Through one hole a dropping-funnel is passed by means of which the acid is introduced, and through the other the exit tube for the gas is passed. The end of the dropping-funnel is drawn out to a capillary, which is bent upwards to prevent loss of carbon dioxide.

The arrangement of the apparatus of Fresenius is shown in Fig. 18. The Erlenmeyer flask should be of about 150 c.c. capacity. The glass tube should be about 70 cm. long and at least 1.2 cm. in diameter. It is inclined slightly so as to allow any water which condenses in its lower half to flow back into the flask. A

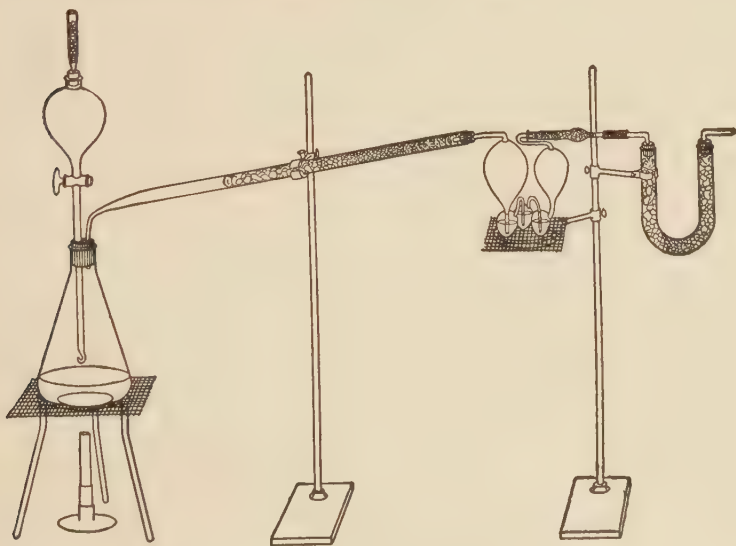


FIG. 18.

wad of glass wool or cotton is pushed down to the centre of the tube, the upper half of which is then filled with granulated calcium chloride, large lumps being first introduced and then the finer material. If this calcium chloride has not already been

saturated with carbon dioxide, a slow stream of the dry gas is passed through the tube for some time and then completely displaced with air.

122. Drying and Absorption of the Carbon Dioxide.—The GEISSLER CAUSTIC-POTASH BULBS are filled two-thirds full with a solution of 1 part of caustic potash and 2 parts of water. The straight calcium-chloride tube is filled with soda-lime and fused calcium chloride, so that the gas leaves the apparatus after passing over the calcium chloride. SODA-LIME is sometimes used for absorbing the carbon dioxide. It is placed in U-tubes, which are weighed before and after absorption of the carbon dioxide. Unless the soda-lime is freshly prepared and somewhat moist the absorption of large amounts of carbon dioxide is somewhat slow, so that two U-tubes are usually required. A calcium-chloride tube must also be attached and weighed. Whether caustic potash or soda-lime is used, an unweighed guard tube filled with calcium chloride must be attached. A small tube filled with soda-lime is also fitted to the dropping-funnel to remove carbon dioxide from the air which is drawn through the apparatus to sweep out the carbon dioxide.

123. Decomposition of the Carbonate.—Dilute sulphuric acid should be used for decomposing the carbonate, provided insoluble sulphates are not formed. When sulphuric acid cannot be used, dilute hydrochloric or nitric acids may be employed. If *sulphides* or *sulphites* are present, chromic acid or a chromate is added to prevent the evolution of sulphuretted hydrogen or sulphur dioxide and sulphuric or nitric acid must be used to decompose the carbonate. When *hydrochloric acid* is used or *chlorides* are present, the carrying of the acid to the absorption bulbs may be prevented by substituting for part of the calcium chloride in the long drying-tube pieces of pumice-stone which have been saturated with copper-sulphate solution and dried at 125°. The method of setting up the apparatus and the details of manipulation are given in Chapter XVI, p. 183, in the determination of carbon dioxide in dolomite.

DETERMINATION OF BORIC ACID BY THE METHOD OF GOOCH.

Considerable difficulty has been met with in determining boric acid, since no insoluble salt of this acid is known which can be washed and weighed accurately without the expenditure of a great deal of labor. The acid can be readily and completely separated from all other acids and bases by distillation with methyl alcohol. The distillate may then be evaporated to dryness and ignited with a known amount of calcium oxide. No boric acid is lost and the amount present is given by the increase in weight of the lime. The details of this method were first published by Gooch.*

124. Apparatus.—The apparatus recommended by Gooch consists of a retort made of a 150-c.c. or 200-c.c. pipette. One of the stems of the pipette, which should have an internal diameter of at least 0.7 cm., is bent into the form of a gooseneck, and is con-

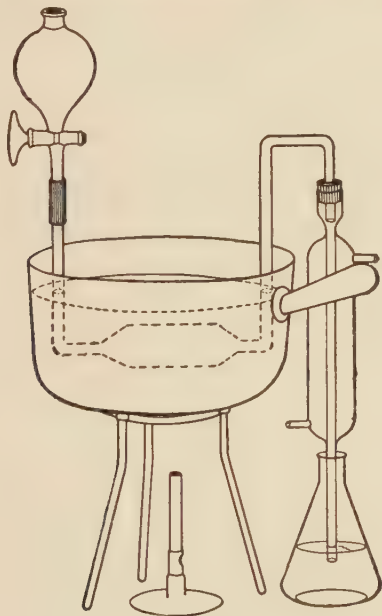


FIG. 19.

needed by means of a rubber stopper with an upright condenser, which in turn is connected by means of a loosely fitting stopper

* *Am. Chem. Jour.*, vol. 9, p. 23.

with an Erlenmeyer flask of about 250 c.c. capacity. The other stem of the pipette is bent at right angles and is connected by means of a short piece of rubber tubing with a small dropping-funnel. An oil- or paraffine-bath is provided of such a size that the retort may be immersed in the liquid.

125. The Solution of the Borate, which should not contain more than 0.2 gram of B_2O_3 , is acidified with nitric or acetic acid.* Hydrochloric acid should be absent, as a considerable amount of this acid would pass over into the lime and be weighed with it unless the solution is neutralized and then acidified with acetic acid. It is better, however, to remove the chlorides with silver nitrate. The filtrate may be distilled directly or the excess of silver nitrate removed with sodium hydroxide or carbonate. Substances insoluble in nitric acid are fused with sodium carbonate. If fluorine is present, it is removed by precipitation as calcium fluoride in the water solution of the fused material.

126. Distillation of the Boric Acid with Methyl Alcohol.—From 1 to 2 grams of calcium oxide are placed in a platinum dish and heated over the blast-lamp until the weight is constant. It is then rinsed with a little water into the Erlenmeyer flask. A large excess of the acetic or nitric acid used to acidify the solution of the borate should be avoided, since these acids volatilize and neutralize the lime. Their salts also form viscous liquids on evaporation. A drop or two of phenolphthalein should therefore be added to the solution and a drop or two of the acid added after the alkaline color of the indicator has been removed. The smaller amounts of calcium oxide may be used when acetic acid is employed. The solution of the borate is transferred to the retort, which is lowered so that at first only the bottom touches the oil or paraffine, which is heated to 130° – 140° . As the liquid distils off the retort is lowered until half of it is immersed and the distillation continued until the water is entirely removed. 10 c.c. of methyl alcohol is then introduced through the dropping-funnel and the solution distilled to dryness. This is repeated five times. If nitric acid has been used to acidify the solution, introduce into the retort 2 c.c. of water between the second and third and between the fourth and fifth additions of methyl alco-

*The small amounts of these acids which distil over into the lime are expelled during the subsequent ignition.

hol and distil to dryness. If acetic acid has been used, add a few drops of this acid with the fourth portion of methyl alcohol.

127. Weighing the Boric Acid.—After the sixth distillation with the methyl alcohol transfer the solution in the Erlenmeyer flask to the platinum dish in which the lime was ignited and weighed. Evaporate the solution to dryness, being careful to avoid spattering. Finally heat the dish with the blast-lamp until constant weight is obtained. The increase in weight is due to B_2O_3 . The residue in the retort may be tested for boric acid by means of turmeric-paper. If nitric acid has been used the nitrous acid should first be oxidized by means of bromine and the excess of the latter expelled.

DETERMINATION OF PHOSPHORIC ACID.

128. Precipitation of Phosphoric Acid as Magnesium-ammonium Phosphate.—Phosphoric acid may be most accurately weighed as magnesium pyrophosphate. The properties of magnesium-ammonium phosphate as well as the magnesium pyrophosphate produced by ignition of this precipitate, have already been discussed under the Determination of Magnesium in Chapter VII, page 85. Only the alkali metals may be present in the solution, as the phosphates of the other metals are insoluble in ammonia and would contaminate the precipitate. Only a moderate amount of ammonium salts should be present, and the solution should be slightly acid with hydrochloric acid. The phosphoric acid is precipitated by adding with constant stirring magnesia mixture in slight excess. This mixture is made by dissolving 55 grams of crystallized magnesium chloride and 70 grams of ammonium chloride in water, adding 300 c.c. of dilute ammonia or 88 c.c. of concentrated ammonia (sp. gr. 0.90) and diluting to 1 liter. After standing for several days, the solution is filtered as required for use. 10 c.c. of this solution is sufficient to precipitate 0.15 gram of P_2O_5 . If the phosphate solution is not distinctly alkaline after the addition of the magnesia mixture, it should be made so by the addition of ammonia. After standing for at least six hours the precipitate is filtered off, washed with water containing one-tenth its volume of strong ammonia, and the precipitate ignited as directed for the determination of magnesium.

129. Separation of Phosphoric Acid as Phosphomolybdate.—If metals other than the alkalis are present, the phosphoric acid must be precipitated from a nitric-acid solution as phosphomolybdate. All of the phosphoric acid is precipitated while the metals are held in solution by the nitric acid, in which the phosphorous precipitate is insoluble. The percentage of phosphoric acid in the precipitate is not constant, but varies within quite wide limits with the conditions of the precipitation. Although by rigidly fixing these conditions a precipitate of sufficiently constant composition for direct weighing can be obtained, more reliable results are obtained by dissolving the precipitate in ammonia, reprecipitating with magnesia mixture and weighing as magnesium pyrophosphate.

130. Removal of Silicic and Arsenic Acids.—Before precipitating the phosphoric acid as molybdate, silicic acid must be removed from the solution by evaporating to dryness and heating at 100° for some time. The dried residue is dissolved in water and nitric acid. Arsenic acid must also be absent except in traces, as this acid forms a precipitate with molybdic acid, which is very similar to the phosphomolybdate. It is also reprecipitated with the magnesia mixture. It may readily be separated from phosphoric acid by passing hydrogen sulphide through the hot hydrochloric-acid solution. As HYDROCHLORIC ACID interferes with the precipitation of the phosphoric acid as molybdate, it must be expelled by evaporation with nitric acid after precipitation of the arsenic, or the separation of the arsenic acid may be delayed until the phosphoric acid has been precipitated by means of magnesia mixture. This precipitate, which will generally contain only a part of the arsenic acid, is dissolved in a little hydrochloric acid, the solution warmed to 70° , and hydrogen sulphide passed for a considerable time. The precipitate is filtered off and washed and the filtrate evaporated to a volume of 50 to 75 c.c. The solution is allowed to cool, a few drops of magnesia mixture are added, and then ammonia, with constant stirring until a slight excess is present. This precipitate is filtered off, washed, ignited, and weighed as usual.

131. Precautions.—The precautions* to be observed in precipitating the phosphoric acid as molybdate are as follows:

* *Zeit. Anal. Ch.*, 28, 141.

Hydrochloric, sulphuric, and boric acids should be absent or present only in small amounts.

Free nitric acid should be present only to the extent of 26 molecules to one molecule of the phosphoric acid. If more than 80 molecules of free nitric acid are present to one molecule of phosphoric acid, the precipitation is incomplete.

The presence of ammonium nitrate hastens the precipitation.

Twice as much molybdic acid must be present as is necessary to form the precipitate; that is, 24 molecules to 1 molecule of phosphoric acid.

132. Precipitation of the Phosphomolybdate.—The solution of the phosphate should be concentrated so that about 0.1 gram P_2O_5 is present in 25 c.c., 0.2 gram P_2O_5 being sufficient for a determination. Enough of a concentrated ammonium-nitrate solution (750 gr. per liter) is added to constitute 15% of the total volume after sufficient molybdate solution has been added to have 80 c.c. present for each 0.1 gram of P_2O_5 . The solution is then heated on the water-bath to 80° – 90° for about ten minutes, and is then allowed to stand for about one hour, when the precipitate may be filtered off and washed. The addition of the ammonium nitrate may be omitted, but more of the molybdate solution must be added, and the solution heated on the water-bath to 60° for from four to six hours. In either case the filtrate should be tested for phosphoric acid by adding more molybdate solution and warming. A white precipitate of molybdic acid must not be mistaken for the yellow phosphate precipitate.

133. Washing the Precipitate.—Various solutions have been used for washing the precipitate, which is not absolutely insoluble, so that the minimum amount of wash-water should be used. Wagner recommends a solution made by dissolving 150 grams of ammonium nitrate in water, adding 10 c.c. concentrated nitric acid, and diluting the solution to one liter. Fresenius recommends the use of a solution made by adding to 100 c.c. molybdate solution 20 c.c. nitric acid (sp. gr. 1.2) and 80 c.c. water. A solution made by diluting the molybdate solution with an equal volume of water is also frequently used.

134. Direct Weighing of the Phosphomolybdate.—When it is desired to weigh the molybdate precipitate, the following slight variations in the method of procedure already given must be ob-

served: Silica must first be completely removed from the solution of the phosphoric acid. After the molybdate has been added, the solution should be heated to about 40° to effect complete precipitation. Serious error results if it is heated to a temperature near 100° . About four hours' digestion at 40° is generally sufficient. The precipitate is filtered off on a Gooch crucible and washed, first with a dilute solution of molybdate until the metals present are removed, and then with water containing 1% of nitric acid until the molybdic acid is removed. The precipitate is then dried in an air-bath heated to 120° . It contains 1.63% of phosphorus.

135. Reprecipitation of the Phosphoric Acid as Ammonium-magnesium Phosphate.—When it is desired to weigh the phosphorus as magnesium pyrophosphate, the molybdate precipitate is washed with the solutions given in par. 133 until the metals present are removed. The beaker in which the precipitation was made, and from which the yellow precipitate need not be wholly removed, is placed under the funnel, the paper is pierced, and the precipitate washed into the beaker with a fine jet of water. The paper is moistened with a little ammonia and washed with hot water, a few drops of ammonia being added if necessary to dissolve the precipitate. Not more than 50 c.c. of wash-water should be used. If the precipitate does not dissolve on stirring the solution, a little more ammonia should be added. Neutralize the solution with strong hydrochloric acid, and if the yellow phosphomolybdate begins to precipitate, add ammonia until dissolved. A white flocculent precipitate insoluble in ammonia is probably silica, and should be filtered off. The solution is again rendered slightly acid with hydrochloric acid and enough magnesia mixture added to precipitate the phosphoric acid present, using 10 c.c. for 0.1 gram P_2O_5 . The solution is neutralized by adding ammonia while stirring constantly. A moderate excess of ammonia is added and the solution is allowed to stand for at least four hours. The precipitate is filtered off, washed with dilute ammonia, ignited, and weighed as usual. Heating with the blast-lamp for ten minutes is advisable, in order to expel any molybdic acid which may have been carried down with the magnesia precipitate.

ANALYSIS OF ALLOYS.*

CHAPTER X.

ALLOYS OF SILVER, LEAD, COPPER, BISMUTH, CADMIUM, AND TIN.

136. Reasons for Analysis of Pure Salts.—In the determinations given in the preceding chapters pure compounds were taken for analysis. This method of procedure serves two purposes. In the first place the exact composition of the compounds being known, the error in a given determination can easily be ascertained. In the second place no error can arise from the contamination of a precipitate with foreign material other than the reagents used. When the student has acquired proficiency in the comparatively simple processes of analyzing pure compounds, he must undertake the determination of elements when existing in combination with each other. It is evident that the determination of iron by precipitation with ammonia is impracticable if aluminium or chromic salts are present.

137. Difficulty of Complete Separation of Elements.—Although calcium is the only metal which can be quantitatively precipitated as oxalate, yet it is by no means true that this element can be separated as oxalate from a solution containing all other metals without carrying many of these down with it. This is due to the fact that most of the oxalates are soluble with difficulty. All of the *sulphates* except those of barium, strontium, and lead are quite soluble, and yet when such soluble sulphates as those of iron or aluminium are present the determination of sulphuric acid by precipitation with barium chloride presents difficulties

* The alloys and minerals whose analyses are given in this and the following chapters have been selected so as to afford practice in the separations required in the analysis of commonly occurring substances. The elements mentioned as occurring in a given alloy or mineral are those commonly found. Some of these are at times absent, while others not listed may be present.

which have been the subject of investigation by many ingenious workers for more than half a century. As the great majority of the substances with which the chemist is called upon to deal are complex rather than simple, a careful study of the separation of the elements is of the greatest importance. Only by the closest attention to details can success be attained in the analysis of complex substances. The importance of testing precipitates for impurities and the solution for unprecipitated portions of an element cannot be too strongly urged. Only in this manner can the accuracy of an analysis be assured.

138. Limit of Accuracy in Analysis.—If a complete analysis is made the sum of all the constituents must be very close to 100%. A summation which is within .5% can generally be obtained if the analysis is conducted with care and reliable methods are used. In general the analysis of an unknown substance should be conducted in duplicate. If the duplicate results do not agree within .2 or at most .3%, a third analysis should be made. As the error of most determinations is at least .1%, it is unnecessary to calculate results to more than hundredths of per cent. As the error in each determination of the analysis of a given substance may be either plus or minus, the practice of dividing the difference between the summation and 100% among the various determinations is not justifiable.

It is in some cases possible to analyze a substance in such a manner that the results are accurate to the hundredth of a per cent. Such results may be computed to the .001 of a per cent. This practice is common in the analysis of metals. Large quantities of the metal are taken, so that considerable quantities of the impurities which are present in small amounts are obtained for determination. The results may then be accurate to the hundredth of a per cent. This does not imply a higher degree of accuracy in the determination of a given element than .1 of a per cent. For example, if iron were present in copper to the extent of .5%, a determination of the iron which is accurate to .01% of the impure copper would represent an error of $\frac{1}{50}$ of the amount of iron present in the copper. In giving the results of such analyses the percentage of the main constituent is obtained by difference, so that the summation is exactly 100%.

139. Separation of Silver from Other Metals.—Silver is readily separated from other metals by precipitation as chloride. Silver chloride being more insoluble in dilute nitric acid than in water the precipitate is washed with dilute nitric acid. This also serves to dissolve compounds of metals such as bismuth and antimony, which tend to form insoluble basic salts. As silver chloride is soluble in mercuric nitrate enough hydrochloric acid must be added to convert all of the mercury present into chloride. This metal must be present in the mercuric condition. The small amount of silver remaining in solution is subsequently precipitated with the mercury as sulphide and may be separated by volatilization of the mercury. If lead is present the solution must be dilute and hot, and no more hydrochloric acid added than just sufficient to precipitate the silver. The silver chloride must be thoroughly washed with hot water. If sodium acetate is added the lead is more easily kept in solution.

EXERCISE 25.

Analysis of a Silver Coin.

Alloy of Copper and Silver.

Prepare two Gooch crucibles for weighing silver chloride. They may be marked 1 and 2 with a blue pencil* and the marks made permanent by heating to redness with the blast-lamp. While the crucibles are drying on the hot plate the following operations should be carried out:

140. Dissolving the Alloy.—Clean a dime thoroughly by rubbing with sand or "Sapolio." Cut into pieces and weigh carefully a piece of about one-half gram. Place in a 200-c.c. beaker and add about 5 c.c. concentrated nitric acid and an equal bulk of water. Cover the beaker with a watch-crystal and warm on the water-bath until the metal is converted into nitrate. Dissolve the residue in water. A little *gold* is sometimes present and will remain undissolved at this point. The solution of silver and copper is decanted into a 300-c.c. Erlenmeyer flask and the gold washed by decantation five or six times, using about 25 c.c. of water each time. The gold is now transferred to a small filter-paper, which is washed with hot water until free from silver. The moist paper is transferred to a weighed porcelain crucible, burned in the usual manner, and the gold weighed. As the amount of gold is always small, it is best to collect on the same paper the gold from all of the weighed portions of the dime, which are dissolved separately in nitric acid to obtain duplicate determinations of the silver and copper. The paper is washed free from silver after each precipitate has been transferred to it.

* A pen. il made for marking on glass, porcelain, etc., is used for this purpose

141. Silver.—The volumes of the solutions of silver and copper in the Erlenmeyer flasks should not much exceed 200 c.c. By proper manipulation this result can easily be secured. Heat nearly to boiling and precipitate the silver by adding hydrochloric acid, drop by drop, with vigorous shaking of the flask. Add only a slight excess of hydrochloric acid and digest the precipitate on the water-bath with occasional vigorous shaking until the solution is very nearly clear. Decant the clear liquid through the weighed Gooch crucible and wash the precipitate two or three times by decantation with about 50 c.c. of hot water to which a few drops of nitric acid have been added. The precipitate should be digested each time for a few minutes on the water-bath. Finally transfer the precipitate to the crucible and wash with hot water containing a little nitric acid until the wash-water gives no precipitate with hydrogen sulphide. Dry the precipitate on the hot plate and weigh.

142. Copper.—Ignite and weigh a Rose crucible. Heat the copper solution, the volume of which should be about 400 c.c., nearly to boiling and saturate with hydrogen sulphide. Filter immediately and wash with water containing hydrogen sulphide. Test the filtrate and wash-water for copper by passing hydrogen sulphide. Dry the precipitate, detach from the paper, burn the latter, and ignite the precipitate in the Rose crucible in a stream of dry hydrogen after the addition of sulphur.

143. Division of Coin Volumetrically.—If there is available a 250-c.c. flask and a 50-c.c. pipette which have been carefully calibrated against each other, the division and weighing of the coin may be carried out in the following manner. The coin is weighed after thorough cleansing. It is then placed in a 200-c.c. beaker and treated with 10 c.c. concentrated nitric acid and an equal bulk of water. The beaker is covered with a watch-crystal and warmed on the water-bath until the metal is converted into nitrate. The watch-crystal is rinsed off and the solution is evaporated to dryness on the water-bath. The residue is dissolved in water, the gold, if present, filtered off and weighed, the filtrate and washings being allowed to flow into the 250-c.c. flask. Finally the solution in the flask is diluted to the mark with water, thoroughly shaken, and 50-c.c. portions taken out with the pipette. The analysis of these portions is carried out as already directed.

The duplicate determinations of silver and copper should agree within about .2%. American silver coins contain very nearly 90% of silver and 10% of copper.

144. Economizing Time.—In carrying out this and subsequent exercises the work should be carefully planned to economize time. Crucibles should be prepared and weighed during the intervals when precipitates are digesting, filtering, or drying, so that the latter may be transferred and weighed without delay.

Two precipitations and filtrations can be carried out at the same time just as readily as one. As experience is gained, a greater and greater number of analyses can be carried on simultaneously. Careful and systematic marking of beakers, funnels, etc., is absolutely necessary. All weights must be recorded in the note-book under systematic headings and numbering of duplicate analyses.

145. Separation of Tin as Stannic Oxide.—Tin is usually separated from other metals as the dioxide SnO_2 . On treating an alloy containing tin with nitric acid, most of the metals form nitrates, while the tin is converted into the dioxide, which remains undissolved on treating the residue with water. If **ANTIMONY** or **ARSENIC** is present more or less of these elements, depending on the amount present, will remain with the tin. Besides these elements, which one would expect from the nature of their oxides to remain undissolved by water or dilute acids, small portions of *copper, lead, bismuth, iron, manganese, and zinc* remain with the stannic oxide and cannot be removed by digestion with dilute nitric acid. In the absence of more than traces of arsenic and antimony the stannic oxide is filtered from the nitric-acid solution, washed with dilute nitric acid, ignited and weighed.

146. Purification of the Stannic Oxide.—The weighed precipitate is then fused in a porcelain crucible with six times its weight of equal parts of sodium carbonate and sulphur, or with the same weight of dry sodium thiosulphate. By this treatment the metals present are converted into sulphides. On treating the fused mass with hot water the sulphides of tin, arsenic, and antimony and a small amount of copper if this element is present dissolve as thio salts of sodium, while the sulphides of the other metals remain and may be filtered off. On treating the insoluble sulphides with warm dilute hydrochloric acid, copper sulphide remains undissolved and may be ignited and weighed as CuO . In the filtrate the lead may be precipitated with sulphuric acid and weighed as sulphate. The iron is precipitated with ammonia, while the zinc is separated from the manganese by passing hydrogen sulphide through the slightly acid solution. The manganese may be precipitated with hydrogen peroxide and weighed as Mn_3O_4 . The weight of any or all of these metals computed as oxide is deducted from the weight of the impure stannic oxide.

If several of these metals are present in the alloy it is perhaps easier and fully as accurate to omit weighing the impure stannic oxide, but fuse it immediately as already described for its purification. The insoluble sulphides are dissolved in a little nitric acid and added to the nitric acid solution of the alloy. The solution of sodium sulphostannate is nearly decolorized by boiling with the addition of pure caustic soda and hydrogen peroxide. The tin is precipitated as sulphide by acidifying with hydrochloric acid. The precipitate is filtered off and washed with water containing ammonium acetate and a little acetic acid. It is then treated with a little concentrated ammonium carbonate solution to dissolve arsenic sulphide. After washing with water the sulphides of tin and antimony are dissolved in warm concentrated hydrochloric acid. Any antimony which is present may be precipitated by digesting the diluted solution with metallic iron. The tin in the filtrate from the antimony is precipitated with hydrogen sulphide and washed. The precipitate is dried and detached from the paper, which is burned. It is then placed in a porcelain crucible and gently heated until sulphur dioxide ceases to be given off. It is then strongly heated after the addition of ammonium carbonate and weighed as stannic oxide, SnO_2 .

147. Separation of Lead as Sulphate.—Lead is most frequently separated from other metals by precipitation as sulphate. The nitric acid solution is evaporated with excess of sulphuric acid until the nitric acid is completely expelled, which is indicated by the evolution of dense white fumes of sulphuric acid. On dilution with water the lead separates out almost completely. In the absence of much bismuth or iron, a more complete precipitation of the lead may be effected by the addition of an equal bulk of alcohol to the dilute sulphuric acid solution. Besides BARIUM and STRONTIUM sulphates which may contaminate the precipitate, BISMUTH may be present as an insoluble basic sulphate. To keep the bismuth in solution considerable sulphuric acid must be present and the precipitate must be washed with dilute (10%) sulphuric acid, which is finally removed by washing with dilute alcohol.

148. Separation of Lead as Chloride from Bismuth.—The precipitate of lead sulphate may be tested for bismuth by warming with concentrated hydrochloric acid. After allowing to cool,

50 c.c. absolute alcohol is added to the solution of lead chloride, the volume of which should be about 5 c.c. The bismuth chloride dissolves in the alcohol and may be filtered off from the precipitated lead chloride. A small amount of the lead dissolves in the alcohol with the bismuth. The latter may be precipitated by largely diluting the alcoholic solution. This method may also be used for separating the lead and bismuth in the nitric-acid solution of lead and bismuth alloys. Before the addition of the alcohol the nitric acid is expelled by evaporating twice with 20 c.c. concentrated hydrochloric acid. The lead chloride may be collected on a Gooch crucible, washed with alcohol, and dried for three hours at 150° and weighed. About 1 mg. of lead chloride remains in the alcoholic solution. The bismuth is precipitated as BiOCl by largely diluting the alcoholic solution and neutralizing most of the hydrochloric acid with ammonia if a large excess is present. It may be washed with water containing a few drops of hydrochloric acid, dried at 110° and weighed.

149. Separation of Lead from Antimony and Barium.—If considerable antimony is present the alloy is dissolved in a rather small amount of nitric acid (4 c.c.) with the addition of tartaric acid (10 grams) and water (5 c.c.). The lead is precipitated by the addition of 4 c.c. concentrated sulphuric acid and diluting the solution to about 250 c.c.

If barium is present, as when minerals are analyzed, so that the sulphate of lead is contaminated with barium sulphate a separation may be effected by digesting the precipitate with ammonium carbonate solution. The sulphate of lead is converted into carbonate, while the barium sulphate is unaffected. The precipitate is filtered off and washed with ammonium carbonate solution, then with water until the wash-water no longer contains sulphates. The lead carbonate is then dissolved with dilute acetic or nitric acid. In this method of separation a little lead is lost on account of the slight solubility of lead carbonate in solutions of ammonium salts. It may be recovered by passing hydrogen sulphide through the ammonium carbonate solution.

EXERCISE 26.

Analysis of Soft Solder.

Alloy of Lead and Tin, Generally containing Small Amounts of Arsenic, Antimony, Iron, and Zinc.

150. Solution of the Alloy.—One gram of the alloy is weighed out and transferred to a beaker of about 500 c.c. capacity. 10 c.c. of concentrated nitric acid and 5 c.c. of water are added. The beaker is covered with a watch-crystal and heated on the water-bath until the alloy is completely decomposed and the nitrous fumes are entirely expelled. 100 c.c. of water is added and the solution boiled for five minutes and allowed to settle for one hour. The stannic oxide is filtered off and washed with hot water. The moist precipitate may be introduced into a weighed porcelain crucible, the paper burned in the usual manner, and finally heated to redness for ten minutes.

151. Tin.—When the precipitate has been brought to constant weight, it is fused with six times its weight of a mixture of equal parts of sulphur and sodium carbonate. The fused mass is dissolved in hot water and the solution filtered. The insoluble sulphides are washed with hot water and treated with a little dilute hydrochloric acid and the paper washed with water. If COPPER is present it will remain on the paper and the small amount present may be weighed as CuO after burning the paper in a porcelain crucible and igniting the precipitate. The LEAD is precipitated by the addition of a few drops of sulphuric acid and 25 c.c. of alcohol to the solution, which should not exceed 50 c.c. After standing one hour, the precipitate is filtered off on a Gooch crucible, washed with alcohol, dried on the hot plate, and weighed. The filtrate is evaporated until the alcohol is completely expelled. Any IRON present is precipitated with ammonia and weighed. Hydrogen sulphide is passed through the filtrate to precipitate any ZINC present, which is filtered off. The filtrate from the insoluble sulphides will contain the tin as a thiostannate and part of the ANTIMONY present in the alloy as a thioantimonate. The solution is boiled after the addition of caustic soda and hydrogen peroxide until it is nearly decolorized. On acidifying and passing hydrogen sulphide both metals are precipitated as sulphides. If antimony is present the metals should be separated by the method given in section 178, page 141. The weight of the impurities found, computed as oxides, is deducted from the weight of the stannic oxide.

152. Lead.—The filtrate from the stannic oxide is transferred to a porcelain dish, 5 c.c. concentrated sulphuric acid added, and evaporated until fumes of sulphuric acid are evolved. Cool the dish by floating it in cold water and add cautiously 75 c.c. of water. Stir thoroughly and add 25 c.c. of alcohol. Allow the solution to stand for at least one hour, filter off the lead sulphate on a weighed Gooch crucible, wash with alcohol until free from acid, dry on the hot plate, and weigh.

153. Arsenic and Antimony.—The alcohol is completely expelled from the filtrate by evaporation and any arsenic present precipitated by passing hydrogen sulphide. If this precipitate is of an orange color instead of pure yellow, antimony is present. It should be filtered off and washed with water containing a little hydrochloric acid until free from iron and hydrogen sulphide. It is then washed with small portions of concentrated ammonium carbonate solution until the arsenic sulphide is entirely dissolved. The arsenic is reprecipitated by acidifying the solution with hydrochloric acid and passing hydrogen sulphide. It is filtered off on a Gooch crucible and washed with water containing hydrogen sulphide and a little hydrochloric acid. The water is removed by alcohol and the precipitate digested with carbon disulphide until sulphur is entirely removed. The arsenic sulphide is dried at 100° and weighed. If antimony is absent the treatment with ammonium carbonate is omitted, the precipitate being filtered off on a Gooch crucible, washed, dried, and weighed. If antimony is present it is ignited and weighed as directed in section 179, page 141.

154. Iron.—A few drops of bromine water are added and the solution is boiled to oxidize the iron and to expel the hydrogen sulphide. The iron is then precipitated by making the filtrate alkaline with filtered ammonia and warming for a few minutes. It is filtered off on a small paper and dissolved by adding a few drops of dilute hydrochloric acid. The paper is washed with about 75 c.c. of water in small portions. The iron is reprecipitated and filtered on the same paper after moistening with a few drops of ammonia. After washing free from chlorides, the moist paper is transferred to the weighed platinum crucible and ignited.

155. Zinc.—Hydrogen sulphide is passed into the combined filtrates to precipitate any zinc present, which is filtered off, washed, and weighed as sulphide.

EXERCISE 27.

Analysis of Rose's Metal.

Alloy of Lead, Bismuth, and Tin, Generally containing Small Amounts of Copper, Arsenic, Antimony, Iron, and Zinc.

One gram of the metal is weighed out and decomposed with nitric acid as directed in Exercise 26. The STANNIC OXIDE is weighed and the impurities determined as directed in the same exercise.

156. Lead.—To the filtrate from the stannic oxide containing the nitrates of lead and bismuth, 5 c.c. concentrated sulphuric acid is added. The solution is evaporated in a porcelain dish until sulphuric-acid fumes are given off. The dish may be placed on the hot plate, sand-bath, or wire gauze and the liquid heated to just below the boiling-point to avoid spattering. When the acid becomes concentrated, the heat may be somewhat increased. The hot concentrated solution is diluted by slowly pouring it with constant stirring into about 100 c.c. of water and digested hot for about half an hour with occasional stirring. The lead sulphate is then filtered off on a

Gooch crucible, washed with 10% sulphuric acid until the wash-water no longer gives a precipitate on making it alkaline with ammonia, adding ammonium carbonate, and warming. The sulphuric acid is then washed out with alcohol. The precipitate is dried and weighed. It is tested for a possible contamination with bismuth as follows: It is dissolved in 5 to 10 c.c. of warm concentrated hydrochloric acid and 50 c.c. of absolute alcohol are added to the solution. After standing for a few moments, the solution, containing the bismuth as chloride, is filtered off. By nearly neutralizing with ammonia, and largely diluting with water, the bismuth is precipitated as oxychloride and may be washed with water containing a few drops of hydrochloric acid, dried, and weighed.

157. Bismuth.—In the filtrate from the lead sulphate, the bismuth is precipitated by just neutralizing with filtered ammonia, adding a few drops of ammonium carbonate, and warming the solution gently for about fifteen minutes. The precipitate is filtered off and washed a few times with water. To free the precipitate from a small amount of basic sulphate it is dissolved in a small amount of dilute nitric acid and reprecipitated. The precipitate is washed with water containing a little ammonium nitrate and dried. It is removed from the paper as completely as possible and placed on a watch-crystal. The paper is replaced in the funnel, moistened with a few drops of dilute nitric acid, and washed with small amounts of warm water. The wash-water is evaporated to dryness in a fairly large weighed porcelain crucible, and the residue ignited until the nitric acid is completely expelled. The main portion of the precipitate is now added, heated with the Bunsen burner and weighed as Bi_2O_3 .

158. Copper.—If copper is present in the alloy, it will be contained in the two filtrates from the bismuth precipitate. Combine these filtrates, acidify with hydrochloric acid, and concentrate to a convenient bulk. Pass hydrogen sulphide through the warm solution, filter, and wash with water containing hydrogen sulphide. Even if copper is absent, a small black precipitate of bismuth sulphide will be obtained at this point because of the slight solubility of the bismuth hydroxide or carbonate. The precipitate may be tested for bismuth by treating with a little dilute hydrochloric acid and diluting the filtrate. A white precipitate indicates bismuth. The copper sulphide being insoluble in dilute hydrochloric acid remains on the paper and may be ignited together with the paper and weighed as oxide. If ARSENIC, ANTIMONY, IRON, or ZINC are present they are separated and determined by the methods given in Exercises 26 or 28.

159. Separation of Copper and Cadmium.—Cadmium may be separated from copper by passing hydrogen sulphide through or adding ammonium sulphide to a solution of the two metals in potassium cyanide. In such a solution copper sulphide is soluble, while cadmium sulphide is not. Silver, bismuth, and lead must be absent, as these metals would be precipitated with the cad-

mium. Cadmium may also be separated electrolytically from copper. The latter metal may be deposited from a solution containing 5% of acid by a current having a tension not exceeding 1.85 volts. Under these conditions cadmium is not precipitated.

EXERCISE 28.

Analysis of Wood's Metal.

Alloy of Lead, Bismuth, Tin, and Cadmium, Generally containing Small Amounts of Copper, Arsenic, Antimony, Iron, and Zinc.

One gram of the metal is weighed, dissolved in nitric acid, and the STANNIC OXIDE weighed and purified by the method given in Exercise 26. The filtrate from the tin is evaporated to dryness on a water-bath. The nitrates are converted into chlorides by evaporating twice on the water-bath to a small bulk after the addition of 20 c.c. of concentrated hydrochloric acid.

160. **Lead.**—After cooling, 25 c.c. absolute alcohol are added. The mixture is stirred and after standing some time the chloride of lead is filtered off on a Gooch crucible, and washed with an ice-cold mixture of 4 parts of 95% alcohol and 1 part of concentrated hydrochloric acid. It is dried on the hot plate or at 150° for three hours and weighed.

161. **Bismuth.**—The filtrate is diluted with about one-half liter of water and nearly neutralized with ammonia (about 40 c.c. of dilute ammonia will be required). After standing twenty-four hours the bismuth oxychloride is filtered off on a Gooch crucible, washed with water containing a few drops of dilute hydrochloric acid, dried at 110°, and weighed as BiOCl.

The bismuth may also be precipitated as bismuth hydroxide by volatilizing most of the alcohol, neutralizing with ammonia, and warming gently. If IRON is present this precipitate will be reddish. In that case it is best to dissolve it in hydrochloric acid and precipitate the bismuth as oxychloride. The bismuth hydroxide is ignited and weighed as oxide, Bi₂O₃.

162. **Cadmium.**—The filtrate from the bismuth oxychloride is evaporated to a bulk of 200 or 300 c.c. If the bismuth has been precipitated by means of ammonia, the filtrate is first acidified with hydrochloric acid and evaporated to a moderate bulk. The solution is saturated with hydrogen sulphide and the precipitate filtered off and washed with water containing hydrogen sulphide. If the cadmium sulphide is dark colored or black, traces of lead or bismuth sulphides may be present because of incomplete separations, or copper may have been present in the alloy. Any arsenic which may have been in the alloy or a trace of tin or antimony will also be present in this precipitate.

163. **Arsenic, Antimony, and Tin.**—It should be tested for these three elements by pouring over it a few drops of warm potassium or sodium sulphide and washing two or three times with warm water, being careful

to stir up the precipitate with the stream of water from the wash-bottle. A precipitate formed on acidifying the filtrate indicates the presence of arsenic, antimony, or tin. If the characteristic orange color of antimony is absent, the supernatant liquid should be decanted and the precipitate warmed with a little concentrated hydrochloric acid. If it dissolves completely, arsenic is absent and the tin may be reprecipitated by diluting and passing hydrogen sulphide. After washing, the moist precipitate with the paper may be burned and the sulphide of tin converted into oxide by ignition. If arsenic or antimony is present, it may be determined as directed in the following exercise.

164. Separation of Copper and Cadmium.—To dissolve out any copper which may be present with the cadmium sulphide, a few drops of potassium cyanide should be poured over the precipitate. It should be thoroughly stirred up with water and washed a few times. If a considerable amount of copper is present, the bulk of the precipitate should be transferred to a beaker by washing out the paper while still in the funnel with a stream of water. The remainder of the precipitate on the paper is dissolved by washing with a little warm dilute nitric acid. The paper is then thoroughly washed with small portions of hot water. The washings are allowed to flow into the beaker containing the main portion of the precipitate. The beaker is warmed and more nitric acid is added if necessary to dissolve the precipitate. The solution is neutralized with sodium carbonate and a slight excess of potassium cyanide added. A small white precipitate at this point may be lead or bismuth carbonates, which should be filtered off and determined. On passing hydrogen sulphide through the filtrate, the cadmium is precipitated as sulphide and may be filtered off on a Gooch crucible and washed with water containing a little hydrogen sulphide. It is finally washed with pure water and the free sulphur extracted by washing with alcohol and then with carbon disulphide. The precipitate is dried at 100° and weighed.

165. Copper.—The filtrate from the cadmium sulphide contains the copper and is acidified* with sulphuric acid and a little nitric acid and evaporated to fumes. The residue is dissolved in water, filtered if necessary, and the copper precipitated as sulphide. If it is small in amount it may be ignited and weighed as oxide. If considerable copper is present, it must be ignited with sulphur in a stream of hydrogen and weighed as cuprous sulphide, Cu_2S . When much copper is present, it is better to determine it electrolytically.

166. Separation of Iron and Zinc.—The filtrate from the first precipitation with hydrogen sulphide (§ 162) contains any zinc or iron which may have been present. These metals may be determined as described for the

* This should be done under a hood with good draught to avoid any possibility of inhaling the very poisonous hydrocyanic-acid fumes.

similar filtrate in Exercise 26. They may also be separated in the following manner:

The solution is boiled to expel hydrogen sulphide, neutralized with ammonia, and acidified with acetic acid. Hydrogen sulphide is passed for some time and the solution allowed to stand for several hours. The clear liquid is carefully decanted through a filter-paper, and after replacing the beaker containing the clear filtrate with another beaker, the sulphide of zinc is brought on the paper and washed with water containing ammonium acetate and acetic acid. The precipitate is dissolved in a little dilute nitric acid and the paper washed with hot water. The solution of the zinc is evaporated to dryness in a weighed porcelain crucible, ignited finally over the blast-lamp to decompose any zinc sulphate which may have been formed, and weighed as oxide. The filtrate is boiled to expel the hydrogen sulphide. A little nitric acid is then added to oxidize the iron, which is precipitated with ammonia and weighed as oxide. A very convenient method of oxidizing the iron and removing the hydrogen sulphide is by the use of bromine water. The bromine should be added until the solution is colored, indicating complete oxidation of the iron and the presence of an excess of bromine. If a solution of bromine in concentrated hydrochloric acid is used a few drops will suffice and the solution will not be diluted to any extent. If manganese is to be removed together with iron, the presence of an excess of bromine is advantageous; otherwise it must be boiled out. As the bromine oxidizes hydrogen sulphide in the cold, the excess of the latter need not be boiled out.

CHAPTER XI.

ANALYSIS OF ALLOYS CONTAINING ARSENIC, ANTIMONY, AND TIN.

SEPARATION OF ARSENIC, ANTIMONY, AND TIN.

167. F. W. Clarke's Method.—A large number of methods have been proposed for the separation of arsenic from antimony and tin. One of the best is that of F. W. Clarke.* *It is based on the fact that stannic sulphide is not precipitated by hydrogen sulphide from a boiling solution of oxalic acid.* The sulphides of arsenic dissolve slightly, and the sulphide of antimony still more so, in boiling oxalic-acid solutions, but both of these elements are completely reprecipitated by hydrogen sulphide. Free mineral acids must be absent from the solution. At least 20 parts of crystallized oxalic acid must be present for 1 part of tin, and the solution should be diluted to 125 c.c. for each 0.1 gram of antimony present. Hydrogen sulphide is passed through the boiling solution for at least one-half hour. The precipitate must be filtered off immediately, as stannic sulphide separates out on standing. The precipitate generally contains a little stannic sulphide. After filtering off and washing two or three times it is dissolved in a little ammonium sulphide and the solution poured into excess of hot strong solution of oxalic acid. Hydrogen sulphide is passed through the boiling solution for ten minutes. The precipitate is now free from tin, and is filtered off and washed with hot water. The oxalic-acid solution of the tin is evaporated down with the addition of sulphuric acid until the oxalic acid is decomposed. The tin may then be precipitated with hydrogen sulphide and weighed as oxide.

168. Separation of Arsenic and Antimony.—The sulphides of arsenic and antimony may be separated by treatment with a *saturated ammonium-carbonate* solution which dissolves the arsenic

* Chem. News, 21, 124.

easily and the antimony only slightly. No more ammonium-carbonate solution than necessary to dissolve the arsenic sulphide should be used. The precipitate, which must first be washed entirely free from hydrogen sulphide, should be treated with small portions of the carbonate solution until no more arsenic is dissolved, as indicated by the absence of a precipitate on acidifying the filtrate. The arsenic is completely precipitated by acidifying with hydrochloric acid, warming, and passing hydrogen sulphide. This method of separating arsenic and antimony is especially applicable if the amount of arsenic present is small.

A better separation of the arsenic and antimony may be effected by dissolving the sulphides in *concentrated hydrochloric acid* with the addition of small amounts of potassium chlorate. The solution is warmed to expel the chlorine, but not to boiling, so as not to melt the sulphur which is generally liberated. It is filtered through asbestos, which is washed with concentrated hydrochloric acid. It is cooled in ice-water and *hydrogen sulphide* passed for one hour. The arsenic is precipitated as As_2S_5 and is washed with strong hydrochloric acid and then with hot water. Antimony remains in solution as trichloride. This method also serves for the SEPARATION of ARSENIC and TIN, the latter behaving like antimony. According to Neher,* for this separation the solution should contain 1 volume of water to 2 volumes of concentrated hydrochloric acid (sp. gr. 1.20). If a stronger acid is used, the precipitation of the arsenic is hindered.

The arsenic is best dissolved and reprecipitated as *magnesium ammonium arsenate*. If hydrogen peroxide is at hand which is free from phosphoric acid, aluminium, etc., the arsenic sulphide may be dissolved in a warm mixture of ammonia and hydrogen peroxide. A very excellent solvent is a solution of sodium peroxide in water. The arsenic acid may then be precipitated by means of magnesia mixture. The arsenic sulphide may also be dissolved in strong hydrochloric acid and potassium chlorate or in fuming nitric acid. These oxidizing solutions should be warmed, but not high enough to melt the sulphur which usually separates out. The latter becomes very nearly white when all of the arsenic has been dissolved out. If the sulphur is large in amount or otherwise

* Zeit. f. Anal. Chem., 1893, p. 45.

troublesome, liquid bromine may be added in small portions to dissolve it. This method of precipitation also serves to separate ARSENIC from ANTIMONY. Tartaric acid is added to prevent the precipitation of the antimony.

169. The Separation of the Antimony and Tin in the hydrochloric-acid filtrate from the arsenic is effected as follows: The hydrogen sulphide is decomposed by the addition of a little potassium chlorate or bromine. The antimony is precipitated by digesting the somewhat diluted solution on the water-bath with the addition of pure iron. Iron produced by reduction in hydrogen is best, and in any event it must be free from phosphorus. The precipitation of the antimony is complete in about one-half hour. It forms a black powder. The tin is reduced to the stannous condition. The solution is heated until the iron is nearly dissolved. The antimony is then filtered off on an asbestos filter over which a little iron has been sprinkled, and is washed with boiled water containing considerable hydrochloric acid.

The TIN is precipitated by passing hydrogen sulphide through the filtrate, which for this purpose is diluted, and the bulk of the acid neutralized with ammonia. The stannous sulphide is washed with water containing hydrogen sulphide and a few grams of ammonium sulphate. It is dried, transferred to a weighed crucible, ignited, and weighed as stannic oxide.

The ANTIMONY is dissolved in hydrochloric acid with the addition of a little potassium chlorate. The solution is diluted after the addition of tartaric acid and the antimony precipitated as sulphide and weighed as oxide.

170. H. Rose's Separation of Antimony from Arsenic and Tin.—This method of separation is based on the insolubility of sodium metantimonate. If the substance is metallic, it may be conveniently oxidized by treatment with concentrated nitric acid in a porcelain evaporating-dish or crucible. The material is dried on the water-bath and transferred to a silver crucible, the porcelain dish being rinsed with caustic-soda solution. The contents of the crucible are evaporated to dryness, eight times the bulk of the mass of solid caustic soda added, heated cautiously to avoid spattering until all water is expelled and then fused for some time. The mass is allowed to cool, and is treated with hot water until the fused material is entirely disintegrated. One-third the

volume of alcohol is added and the solution allowed to stand for twenty-four hours with frequent stirring.

If the arsenic, antimony, and tin are obtained by separation as sulphides, they may be dissolved in solution of sodium sulphide and the cold-saturated solution treated with small portions of sodium peroxide until the solution is colorless and oxygen is copiously evolved on the further addition of the peroxide. The solution is boiled and after cooling one-third the volume of alcohol is added. The solution is then allowed to stand for twenty-four hours.

The precipitate obtained by either method is washed, first with dilute alcohol composed of equal volumes of alcohol and water and then with a mixture of one volume of water and three volumes of alcohol. A few drops of sodium carbonate solution are added to each of the washing fluids. If much tin is present, it is advisable to fuse the metantimonate a second time with soda. The antimony is dissolved in hydrochloric acid containing a little tartaric acid, precipitated with hydrogen sulphide, and weighed as oxide.

The filtrate containing the arsenic and tin is acidified with hydrochloric acid and evaporated until all of the alcohol is expelled. The solution is warmed and hydrogen sulphide passed until precipitation is complete. The arsenic and tin may then be separated by one of the methods already given.

171. Electrolytic Separation of Antimony from Arsenic and Tin.—Antimony may also be separated electrolytically from arsenic and tin, according to Classen.* The arsenic must be present as *arsenic acid*, otherwise a portion of it will be precipitated with the antimony, while the remainder will be oxidized to arsenic acid. A saturated solution of sodium sulphide must first be prepared. If the commercial sodium sulphide is used it must be dissolved in water and the solution saturated with hydrogen sulphide which has been washed with water and then passed through several tubes filled with cotton wool. While passing hydrogen sulphide the air should be excluded. The solution is filtered and rapidly evaporated in a large platinum or porcelain

* Ber., 17, 2245; 18, 1110; 28, 2160.

dish over the free flame until a thin skin begins to form on top. The hot solution is poured into glass-stoppered bottles, which must be completely filled and immediately well stoppered. The sodium sulphide may also be prepared by completely saturating a solution of pure caustic soda with hydrogen sulphide, filtering, and evaporating down, as already directed.

The sulphides of arsenic, antimony, and tin are transferred to a weighed platinum dish of about 150 c.c. capacity and dissolved in 80 c.c. of the sodium-sulphide solution. Add enough concentrated solution of pure caustic soda to furnish 1 to 2 grams of NaOH. The caustic-soda solution must be clear and give no precipitate with the sodium-sulphide solution. The dish is gently warmed to aid solution. It is electrolyzed at a temperature of 50° to 60° with a current of 0.5 ampere. Precipitation of the antimony is complete in two hours. The watch-crystal is washed with a little water, which is allowed to run down the positive electrode. The solution is removed without interrupting the current, the antimony washed with water and then with alcohol, dried at 80° to 90°, and weighed.

The TIN may be determined by acidifying the filtrate with hydrochloric acid, concentrating to a bulk of 200 or 300 c.c., filtering, if necessary, and passing hydrogen sulphide. The precipitate is washed with water containing hydrogen sulphide and a few grams of ammonium sulphate. It is weighed as stannic oxide.

172. Separation of Arsenic.—Arsenic is very readily separated from other metals as *arsenious chloride*, AsCl_3 . This compound is *very volatile*. When pure it boils at 130°. It is rapidly volatilized when its solution in hydrochloric acid is boiled. Even at temperatures considerably below the boiling-point the arsenic slowly volatilizes. When it is present in its higher state of oxidation, the arsenic is not volatilized on boiling its hydrochloric-acid solution. Various reducing agents have been used to convert the arsenic into the arsenious chloride. The most common among these are ferrous and cuprous salts and hydrogen sulphide. If small amounts of arsenic are present the solution may be distilled after the addition of concentrated hydrochloric acid. On repeating the distillation once or twice after the addition of concentrated hydrochloric acid all of the arsenic will be carried over. If much

arsenic is present, the solution must be saturated with hydrochloric-acid gas and the distillation carried out in a current of this gas.

173. Dissolving Arsenic Compounds.—Various methods of decomposing the ore or other material have been proposed, the objects sought being to prevent the loss of arsenic as trichloride and to leave the hydrochloric-acid solution as free as possible from oxidizing material. If the material is soluble in hydrochloric acid, it may be digested cold with concentrated hydrochloric acid for some time. Liquid bromine may then be added and the solution warmed, at first gently and then more strongly, until the excess of bromine is expelled. The material may also be brought into solution by treatment with concentrated nitric acid, the excess being expelled by evaporation after the addition of a little sulphuric acid. The residue may then be dissolved in concentrated hydrochloric acid.

174. Distillation of the Arsenic.—If the amount of arsenic present is small, the solution may be decanted into the distilling-flask of the apparatus shown in Fig. 20 and the insoluble residue washed with concentrated hydrochloric acid. About 5 grams of ferrous sulphate, or, still better, ferrous chloride or cuprous chloride, are added and 50 to 75 c.c. concentrated hydrochloric acid. The solution is heated to boiling, and when the liquid has boiled down to a volume of about 40 c.c., 50 c.c. concentrated hydrochloric acid is poured through the funnel and the solution again boiled down to 40 c.c. The distillate is received in a beaker or flask containing about 250 c.c. of hydrogen-sulphide water. After the second distillation this beaker is removed and replaced by another containing hydrogen-sulphide water. The distillation is repeated after the addition of 50 c.c. of concentrated hydrochloric acid to the

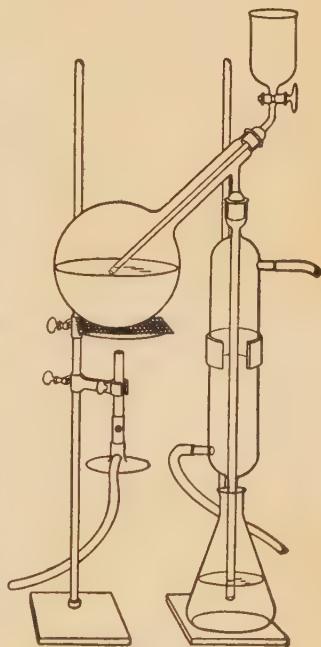


FIG. 20.

flask. A trace of arsenic is sometimes obtained by a fourth distillation.

When LARGE AMOUNTS of ARSENIC must be distilled, the dropping-funnel is replaced by a glass tube leading to a flask in which hydrochloric-acid gas is generated. This gas is very readily obtained by allowing concentrated sulphuric acid to drop into concentrated hydrochloric acid. After transferring the arsenic solution to the distillation flask it is saturated with hydrochloric acid by passing the gas into the solution, which has been cooled to zero by immersing the flask in a vessel filled with cracked ice. When the gas is no longer absorbed, but bubbles through the solution, the ice is removed and the solution brought to a boil. The stream of hydrochloric-acid gas is allowed to flow and the distillation is continued until the volume of the solution is reduced to about 40 c.c. The arsenic may be absorbed in hydrogen-sulphide water and the precipitate of arsenious sulphide filtered off and weighed as such.

EXERCISE 29.

Analysis of Type Metal.

Alloy of Copper, Lead, Antimony, Tin, with Small Amounts of Iron and Arsenic.

175. Solution of the Alloy.—To 1 gram of the alloy, which has been cut into small shavings with a clean knife, or sampled by means of a clean hack saw producing fine “sawings,” is added 15 c.c. concentrated hydrochloric acid. The solution is gently warmed on the water-bath and a drop or two of concentrated nitric acid is added occasionally until solution is affected. All of the metals will be converted into chlorides which will remain in solution with the possible exception of lead chloride. An excess of nitric acid is to be avoided as it tends to form insoluble metastannic acid, which can be readily distinguished from the crystalline lead chloride. If metastannic acid forms, the operation must be repeated, using less nitric acid or adding it less frequently. After a few trials the correct method of adding the nitric acid is soon acquired.

176. Lead.—The solution is allowed to cool and then stand at least $\frac{1}{2}$ hour or better over night to allow the lead chloride to crystallize out. Ten times the volume of absolute alcohol is then added in several portions. After standing for about half an hour, the lead chloride is filtered off on a Gooch crucible, washed with a mixture of 4 parts of 95% alcohol and 1 part of concentrated hydrochloric acid, and finally with pure alcohol. It is dried for three hours at 150° and weighed. The great advantage of this method of separating the lead is that the very troublesome treatment of the sulphides of the metals present with sodium or potassium sulphide is avoided. The *most difficult part* of the operation is the solution of the alloy.

177. Copper and Iron.—The filtrate from the lead chloride is heated until the alcohol is expelled. Two grams of tartaric acid and an excess of ammonia are added and the solution warmed until the precipitate dissolves. By the addition of five c.c. of saturated hydrogen-sulphide water, the copper and the small amount of lead still unprecipitated as well as a trace of iron which may be present may be precipitated without bringing down any of the tin and antimony. The solution is warmed and when the dark colored precipitate has settled, one c.c. of the hydrogen-sulphide water is added to the clear supernatant liquid. If no further precipitate is produced, the solution is filtered and the precipitate washed with water containing hydrogen sulphide.

The precipitate is dissolved in a little warm dilute nitric acid and the lead separated as sulphate, the nitric acid being expelled by evaporation after the addition of sulphuric acid. The copper is precipitated from the filtrate as sulphide and if small in amount may be ignited and weighed as oxide. If considerable copper is present it must be weighed as sulphide or without precipitation as sulphide may be separated electrolytically from the iron. One or two c.c. concentrated nitric acid are added and a current of one-half ampere passed until all the copper is precipitated. The iron may then be precipitated with ammonia and weighed as oxide.

178. Separation of Antimony and Tin.—The solution of antimony and tin is acidified with hydrochloric acid, hydrogen sulphide passed, and the precipitate filtered off and washed two or three times. A hole is made in the point of the filter-paper by means of a glass rod and the bulk of the precipitate washed into a beaker with a little water. Warm dilute hydrochloric acid is poured over the paper to dissolve the portion of the precipitate still adhering to the paper. The precipitate in the beaker is dissolved by warming and adding concentrated hydrochloric acid. The hydrogen sulphide is decomposed by the addition of a crystal of potassium chlorate and warming. Some pure metallic iron is added and the solution heated on the water-bath for about one-half hour or until the iron is nearly dissolved. The precipitated antimony is filtered off on a Gooch crucible, a little iron having been sprinkled on the asbestos. The precipitate is washed with boiled water to which considerable hydrochloric acid has been added.

179. The antimony is dissolved in hydrochloric acid to which a little potassium chlorate has been added. The solution is warmed to expel chlorine and, after the addition of tartaric acid and water, hydrogen sulphide is passed. The antimony sulphide is filtered off and washed with water containing a little hydrogen sulphide. The moist precipitate is rinsed into a capacious porcelain crucible with water. The small portion still adhering to the paper is dissolved in a little warm ammonium sulphide and the solution allowed to flow into the crucible. The solution is evaporated on the water-bath after the addition of a few cubic centimeters of concentrated nitric acid. If sulphur separates, a little liquid bromine is added when the solution has become quite concentrated. When the globule of sulphur has disappeared, expel the excess of nitric acid by heating on the hot plate or with the Bunsen

burner, finally heating to full redness. Cool a little, sprinkle some ammonium carbonate over the precipitate, and ignite again to completely expel sulphuric acid and weigh as antimony tetroxide, Sb_2O_4 .

180. Tin.—To precipitate the tin in the filtrate from the antimony the excess of hydrochloric acid is neutralized with ammonia, the solution diluted somewhat, warmed, and hydrogen sulphide passed until the tin is entirely precipitated. The stannous sulphide is washed with water containing hydrogen sulphide and a few grams of ammonium sulphate. It is dried and detached from the paper which is burned. The precipitate and the ash are placed in a weighed porcelain crucible and heated very gently with free access of air until sulphur dioxide ceases to be given off. The oxidation may be assisted by the addition of a few drops of nitric acid. Finally the precipitate is strongly heated to expel sulphuric acid, which is completely removed by the addition of a little ammonium carbonate and again igniting. It is weighed as stannic oxide SnO_2 .

181. Arsenic.—As only a trace of arsenic is present, a 5- or 10-gram portion of the alloy should be taken for its determination. Dissolve in hydrochloric acid and potassium chlorate and warm to expel the chlorine. Filter off the lead chloride on asbestos and wash a few times with dilute hydrochloric acid. Add one-third the volume of concentrated hydrochloric acid and pass hydrogen sulphide. Filter off the precipitate consisting of the sulphides of copper and arsenic on asbestos, wash with hot water containing hydrogen sulphide and a little hydrochloric acid. Dissolve the arsenic sulphide by washing the precipitate with a little warm dilute ammonia. Evaporate the solution nearly to dryness in a porcelain dish. Oxidize the arsenic by warming with concentrated nitric acid, dilute the solution somewhat, neutralize with filtered ammonia, and add magnesia mixture. After standing twenty-four hours filter, wash, ignite, and weigh as magnesium pyroarsenate according to the directions given in Chapter VII, page 88.

EXERCISE 30.

Analysis of Britannia Metal.

Alloy of Tin, Antimony, and Copper, with Small Amounts of Bismuth; Lead, and Iron.

182. Decomposition of the Alloy by Means of Chlorine.—Alloys containing a large percentage of tin are best decomposed by a stream of chlorine. The method is applicable to alloys containing less than 15% of lead and copper.

A hard-glass combustion-tube 70 cm. long is taken and one end drawn out, making a small tube 20 cm. long, which is bent at right angles. This small tube is connected by means of a cork stopper with a Peligot tube the bulbs of which are nearly filled with dilute hydrochloric acid (1 : 3)

containing about 1 gram of tartaric acid. A second Peligot tube is connected with the first and contains a solution of caustic soda (1 : 3). The chlorine is evolved in a 2-liter flask containing pieces of pyrolusite, over which concentrated hydrochloric acid is poured. The flask is heated on a water-bath. The chlorine is passed through a wash-bottle containing water and then through two wash-bottles containing sulphuric acid. It is then passed into the combustion-tube, connection being made by means of a cork stopper. Wherever rubber is used for making connections, it must be well coated with paraffine. This is also advisable for the cork stoppers. The chlorine is not allowed to pass into the combustion-tube until all of the air has been displaced from the flask and the wash-bottles. All escaping chlorine should be absorbed in caustic-soda solution.

One gram of the alloy in *fine* turnings is weighed out and placed in a porcelain boat which is placed in the middle of the combustion-tube. The chlorine is first allowed to act on the alloy in the cold. When no further action is observed, the part of the tube in which the boat is situated is heated gently with the Bunsen burner, and then more strongly until the contents of the boat fuse. The CHLORIDES of MERCURY, BISMUTH, ARSENIC, ANTIMONY, and TIN VOLATILIZE and are driven out of the tube by heating it gently from the boat to the end which is drawn out. These chlorides are absorbed in the hydrochloric acid contained in the first Peligot tube, while the excess of chlorine is absorbed in the caustic-soda solution contained in the second Peligot tube.

The chlorine in the apparatus is then displaced by means of a stream of dry air or carbon dioxide, the chlorine generator having been removed. The apparatus is disconnected, the boat containing the CHLORIDES of COPPER, LEAD, and IRON is placed in a porcelain dish, and the tube washed out with hot water which is allowed to flow into the dish containing the boat. Hydrochloric acid is added and the dish warmed until the contents of the boat are dissolved. The latter is removed and washed.

183. Lead, Copper, and Iron.—The lead is precipitated by evaporation with sulphuric acid and diluting and is filtered off and weighed as sulphate. The copper is precipitated by means of hydrogen sulphide and weighed as sulphide or determined electrolytically from a nitric acid solution. The iron is precipitated by means of ammonia and weighed as oxide.

The contents of the first Peligot tube are poured into a beaker and the Peligot tube well washed out with water to which hydrochloric acid is added if necessary. The solution is warmed and hydrogen sulphide passed until precipitation is complete. The filtrate should be heated to boiling, strong hydrochloric acid added, and hydrogen sulphide passed again to insure complete precipitation of the arsenic.

184. Bismuth.—If the sulphide precipitate is dark colored, bismuth is present. The precipitate is washed into a beaker, ammonium sulphide added, and the solution warmed. The solution is filtered through the same paper and the precipitate washed with warm water containing a little

ammonium sulphide. The bismuth sulphide is dissolved in a little warm dilute nitric acid and the paper washed. The bismuth is precipitated with ammonia and ammonium carbonate, ignited, and weighed as oxide, Bi_2O_3 .

185. Separation of Tin from Arsenic and Antimony.—The ammonium-sulphide solution of arsenic, antimony, and tin is poured with vigorous stirring into a hot solution of 25 grams of oxalic acid in 200 c.c. of water. The solution is heated to boiling and hydrogen sulphide passed for about fifteen minutes. The precipitate is filtered off immediately and washed with hot water containing hydrogen sulphide. It is dissolved in ammonium sulphide and the treatment with hot oxalic acid and hydrogen sulphide repeated.

186. Tin.—The oxalic-acid solution of tin is evaporated down, with the addition of 5 c.c. concentrated sulphuric acid, to fumes. The solution is cooled, cautiously diluted with water, and hydrogen sulphide passed to insure complete precipitation of the tin. Wash the precipitate with water containing ammonium acetate and a little acetic acid, dry, ignite, and weigh as stannic oxide SnO_2 .

187. Arsenic and Antimony.—The precipitate of arsenic and antimony sulphides is treated with a little concentrated ammonium-carbonate solution and washed to remove arsenic. The antimony is then weighed as oxide according to the directions given in Exercise 29, page 141. The arsenic is determined according to the directions given in the same exercise.

CHAPTER XII.

ANALYSIS OF ALLOYS CONTAINING IRON, NICKEL, AND ZINC.

188. Separation of Zinc as Sulphide.—Zinc may be separated very completely from most metals as sulphide. Hydrogen sulphide passed through the moderately acid solution separates *silver, lead, mercury, bismuth, copper, cadmium, arsenic, antimony,* and *tin* from zinc. On neutralizing the solution almost completely, or making it acid with acetic or citric acid, or a drop or two of a mineral acid, and passing hydrogen sulphide, zinc is precipitated as sulphide, while *cobalt, nickel, manganese, aluminium,* and *iron* remain in solution as well as the *alkaline-earth metals* and the *alkalies*. Zinc may be separated from *chromium* and *aluminium* by adding sodium sulphide to a solution of these metals containing tartaric acid made alkaline with ammonia.

Although the separation of zinc as sulphide from other metals is very perfect and the metal can be weighed with the greatest accuracy as sulphide, the method is not very largely used. This arises from the fact that zinc sulphide is very difficult to filter and wash because of its tendency to pass through the filter-paper. Ignition of a precipitate with sulphur in a stream of hydrogen is also somewhat troublesome. The latter difficulty may be obviated by dissolving the sulphide in hydrochloric or nitric acid and precipitating the zinc as carbonate and weighing as oxide or precipitating as zinc-ammonium phosphate and weighing as zinc pyrophosphate. The zinc sulphide is washed more readily if hydrogen sulphide and ammonium sulphate or acetate are present in the wash-water.

189. Separation of Zinc as Zincate.—Zinc may also be separated from *cobalt, nickel, iron,* and *manganese* by pouring the acid solution of these metals into excess of caustic-soda solution. The zinc hydroxide first precipitated redissolves in the excess of alkali,

forming sodium zincate, while the hydroxides of the other metals are insoluble in the caustic alkali and may be filtered off. Before filtering, the solution should be diluted to precipitate a small amount of cobalt, which dissolves in concentrated caustic-soda solution. The concentrated alkali is also liable to ruin the filter-paper.

The zinc may be precipitated as sulphide by passing hydrogen sulphide through the filtrate. The sulphide obtained in this manner from an alkaline solution coagulates and settles readily and does not tend to pass through the filter-paper. If the hydrogen sulphide is passed too long the zinc sulphide redissolves.* The presence of sodium or ammonium chloride tends to prevent this action. The danger may be avoided by adding hydrogen sulphide water until no more precipitate forms. The alkali is washed out of the precipitate with considerable difficulty, however, and the precipitate also carries down silica. After igniting with sulphur in a stream of hydrogen the alkali may be extracted with hot water and the zinc sulphide again ignited and weighed as sulphide. For determining silica, the zinc sulphide is dissolved in hydrochloric acid and the solution evaporated to dryness. The zinc chloride is dissolved in water and the silica filtered off, ignited, and weighed.

EXERCISE 31.

Analysis of Brass or Bronze.

Alloy of Lead, Copper, Tin, and Zinc, Small Amounts of Arsenic and Iron.

190. Solution of the Alloy.—Weigh out 1 gram of the alloy and place in a 300-c.c. beaker, add 10 c.c. concentrated nitric acid and 5 c.c. water. Cover the beaker with a watch-crystal and place in a dish of cold water. After one-half hour place the beaker on the water-bath and evaporate the solution to dryness. 100 c.c. of boiling water and a few drops of nitric acid are added and the solution boiled for five minutes.

191. Tin.—The stannic oxide is filtered off and washed with hot water. The moist precipitate is introduced into a weighed porcelain crucible and the paper burned in the usual manner. If the amount of tin is small (less than 1%) it is weighed at this point, otherwise it is fused with six times its weight of a mixture of equal parts of sulphur and sodium carbonate. The fused mass is dissolved in hot water and the solution filtered. The *copper*, *lead*, and *iron* which were carried down with the stannic oxide will remain on the paper as sulphides, while the filtrate will contain all of the tin and

* L. W. McCay, Jour. Am. Chem. Soc., 30, 376.

any *arsenic* or *antimony* which may have been present. The insoluble sulphides are dissolved in a little nitric acid, the paper washed, and the solution added to the filtrate from the stannic oxide.

If arsenic and antimony are absent, the tin may be precipitated out of the sodium sulphide solution and weighed. The excess of sulphur should first be removed from the solution by heating to boiling after the addition of caustic soda and then adding hydrogen peroxide in small quantities until the solution is nearly decolorized. It is then acidified with hydrochloric acid while stirring constantly, heated, and hydrogen sulphide passed. The stannic sulphide is washed with hot water containing ammonium acetate and a little acetic acid. It is ignited and weighed as stannic oxide in the usual manner.

192. Arsenic and Antimony.—If arsenic is present in the alloy, a small amount of this element will be present in the sodium sulphide solution of the tin and will be precipitated with the stannic sulphide. It may be removed by treating the precipitate with a little concentrated solution of ammonium carbonate and washing. The solution of arsenic should be added to the nitric acid solution of the alloy.

If antimony is also present in the alloy, the sulphides of arsenic, antimony, and tin must be separated by one of the methods given in Chapter XI, page 141.

193. Lead.—To the filtrate from the stannic oxide 5 c.c. concentrated sulphuric acid are added and the solution evaporated in a porcelain dish until the nitric acid is entirely expelled and white fumes of sulphuric acid are given off. The solution is cooled by floating the dish on cold water and diluted with 75 c.c. of water. After stirring thoroughly, 25 c.c. alcohol are added and the solution allowed to stand for at least one hour. The lead sulphate is filtered off on a Gooch crucible, washed with water containing about 1% of sulphuric acid and 25% of alcohol and then with pure alcohol until free from acid. It is dried on the hot plate and weighed.

194. The copper is best determined electrolytically. The filtrate from the lead sulphate is heated on the hot plate until most of the alcohol is expelled. Two c.c. concentrated nitric acid are added and the warm solution (about 60°) electrolyzed with a current of one-half to one ampere for about six hours.

Hydrogen sulphide is passed through the acid filtrate from the copper to precipitate traces of *arsenic*, *antimony*, or unseparated *tin* which may be present. If more than traces are found, the metals must be separated and determined by the methods given in the preceding exercises. When the amount of copper is large, as is generally the case, it is advisable to divide the solution into two portions for the electrolysis, as about 300 mg. of copper is generally sufficient for a good determination. The solution may be divided by weighing it and then pouring out about half of it and again weighing or the solution may be diluted to a known volume as 250 or 500 c.c. and a portion measured out. The copper may be determined in each portion and the filtrates combined for the zinc determination. For the

duplicate zinc determination the copper may be precipitated as sulphide, **which is filtered off, well washed, and discarded.**

195. Iron.—The filtrate from the copper is boiled to expel hydrogen sulphide and a little nitric acid added to oxidize the iron, which is precipitated with ammonia and weighed as oxide. If more than a small amount of iron is present, the precipitate must be redissolved and reprecipitated to completely separate it from the zinc.

196. Zinc.—The filtrate from the iron is evaporated to small bulk and the zinc precipitated and weighed as pyrophosphate. The zinc may also be precipitated and weighed as sulphide.

EXERCISE 32.

Analysis of German Silver.

Alloy of Copper, Zinc, and Nickel, with Small Amounts of Lead, Iron, and Tin

One gram of the alloy is weighed out and dissolved in nitric acid as directed in the preceding exercise. The *tin*, *lead*, and *copper* are determined as directed in the same exercise.

Hydrogen sulphide is passed through the acid filtrate from the copper to precipitate traces of *arsenic*, *antimony*, *tin*, or unseparated *copper* which may be present. If more than traces are found, the metals must be separated and determined by the methods given in the preceding exercises.

197. Zinc.—The filtrate is boiled until the hydrogen sulphide is expelled and the solution concentrated to a small bulk and the acid nearly neutralized with caustic soda. Five to ten grams of caustic soda are dissolved in about 50 c.c. of water and the solution of zinc and nickel added slowly with constant stirring. The solution is diluted with an equal bulk of water and the precipitate filtered off and washed. The zinc in the filtrate is precipitated with hydrogen sulphide, filtered off, and washed free from alkali. The zinc sulphide is dried and detached from the paper as completely as possible.

The portion still adhering to the paper is dissolved in nitric acid and the solution evaporated to dryness in a porcelain crucible. The remainder of the precipitate is added and the whole ignited with sulphur in a stream of hydrogen. If the precipitate is small it need not be dried, but is immediately dissolved in nitric acid and after evaporation converted into sulphide. The sulphide is tested for alkali by digestion with hot water. If alkali is found it must be completely extracted and the sulphide again weighed after ignition with sulphur in hydrogen. The precipitate is then dissolved in nitric acid and the solution evaporated to dryness. The zinc nitrate is dissolved in water and the silica filtered off, washed, ignited, and weighed. The zinc sulphide may also be dissolved in hydrochloric acid, the zinc precipitated as zinc ammonium phosphate and weighed as pyrophosphate.

198. Iron and Nickel.—If iron is absent, the nickel hydroxide may be washed and after transferring the precipitate to a weighed porcelain crucible

and burning the paper it may be reduced to metallic nickel by heating in a stream of hydrogen and weighed. If iron is present, the precipitate is dissolved in hydrochloric acid and the iron precipitated with ammonia. Unless a very small amount is present it must be redissolved and reprecipitated, and after washing is ignited and weighed as oxide. The nickel is then reprecipitated as hydroxide by means of an excess of caustic soda, reduced in a stream of hydrogen and weighed as the metal.

EXERCISE 33.

Analysis of Manganese-Phosphorus-Bronze.

*Alloy of Copper, Lead, Tin, Zinc, Manganese, Phosphorus (less than 1%),
Traces of Iron.*

199. Solution.—One gram of the alloy is weighed out and dissolved in nitric acid as directed in Exercise 31, page 146. Nearly all of the phosphorus remains with the stannic oxide as a phosphate. After fusing the impure precipitate and separating the impurities as given in Exercise 31, and precipitating the tin as sulphide, the solution containing only the phosphorus as phosphoric acid is discarded, as this element is determined in a separate portion of the alloy.

200. Lead, Copper, and Zinc are determined as given in Exercise 31. The phosphoric acid which did not remain with the stannic oxide will be present in the alkaline solution of the zinc. This element should therefore be precipitated and weighed as pyrophosphate.

201. Iron.—In order to separate manganese and iron from zinc, bromine or hydrogen peroxide is added to the filtrate from the copper. The solution is boiled and excess of ammonium added to redissolve any zinc phosphate which may be precipitated. The precipitate consisting of ferric hydroxide and manganese dioxide is filtered off and washed. It is dissolved in a little hydrochloric acid and the paper well washed. The solution is boiled until the chlorine is completely expelled, then neutralized with ammonia, warmed, and the trace of iron filtered off immediately. Unless the precipitate is very small it is redissolved in hydrochloric acid and again precipitated with ammonia and quickly filtered off and washed. It is ignited and weighed as oxide.

202. Manganese.—The combined filtrates from the iron contain all of the manganese unless the amount of iron present is considerable. The solution should be evaporated to dryness in a porcelain dish and the ammonium chloride volatilized by gently heating with the Bunsen burner. The residue is dissolved in a few c.c. water and a few drops of hydrochloric acid and the manganese precipitated and weighed as sulphide as directed in Exercise 22.

203. Volumetric Determination of Iron and Manganese.—If considerable iron is present, the method of separation given is not applicable. In this case the simplest methods of determining the two metals are volumetric. The ammonium precipitate should be dissolved in sulphuric acid with

expelled by boiling. The solution must be made up to a definite volume and divided into two equal portions. For this purpose a 100-c.c. flask should be used which has been calibrated with a 50-c.c. pipette by emptying the pipette twice into the dry flask and making a mark on the stem. The solution of iron and manganese is evaporated to small bulk, transferred to the flask, made up to the mark and thoroughly mixed. 50 c.c. are withdrawn with the dry pipette. The solution adhering to the walls of the pipette is rinsed out with distilled water and added to the portion remaining in the flask. One of these portions is reduced with zinc and the iron titrated with standard permanganate. (See p. 316.) The other portion is shaken up with zinc oxide until the free acid is neutralized. One gram of zinc sulphate and a drop or two of dilute nitric acid are added and the solution diluted to several hundred cubic centimeters. The manganese is titrated with standard potassium permanganate according to Volhard. (See p. 327.)

204. Phosphorus.—For the determination of phosphorus a 5-gram portion of the alloy is taken, as the percentage of this element is usually small (seldom more than 0.2%). The material is placed in a 200-c.c. beaker and 20 to 30 c.c. concentrated nitric acid added. The beaker is covered with a watch-crystal and after the first violent action of the acid has ceased it is placed on the water-bath and heated until the alloy is completely decomposed and the residue is pure white. All of the phosphoric acid will remain with the tin provided a sufficient amount of the latter is present in the alloy. From six to eight times as much tin as P_2O_5 must be present. Unless at least 5% of tin has been found, a preliminary test should be made by dissolving about a gram of the alloy in concentrated nitric acid, filtering, and testing the filtrate for phosphoric acid with molybdate mixture. If phosphoric acid is found in the filtrate, metallic tin must be added before dissolving the alloy in nitric acid. From one-half to one gram will usually be found sufficient.

The nitric acid solution of the alloy is diluted and the stannic oxide containing the phosphoric acid is filtered off and washed a few times. After drying, the precipitate is transferred to a porcelain crucible, the paper is burned, and the ash added. After adding three times its weight of potassium cyanide, cover the crucible and fuse for a few minutes at a red heat. The stannic oxide is reduced to metallic tin and the phosphoric acid forms potassium phosphate. After cooling, extract the fused mass with hot water, filter, and wash the paper with hot water.

Expel the hydrocyanic and cyanic acids by boiling with concentrated hydrochloric acid. *This operation must be conducted under a hood with good draught.* Evaporate to dryness to dehydrate the silicic acid which has been dissolved from the porcelain by the action of the potassium cyanide. Dissolve the dry residue in a little hydrochloric acid and pass hydrogen sulphide to precipitate a small amount of tin and copper which is present. Filter, wash the precipitate, and destroy the hydrogen sulphide in the fil-

trate by adding bromine water and boiling. If the volume of the solution exceeds 50 c.c., concentrate by boiling. Cool and precipitate the phosphoric acid by adding about one-half gram of crystallized magnesium chloride or sulphate dissolved in a little water and then neutralizing the solution with filtered ammonia while stirring vigorously. Add a small excess of ammonia. Assure yourself that the phosphoric acid is all precipitated by adding a little magnesia mixture to the clear supernatant liquid. After standing several hours, filter, wash with dilute ammonia, ignite in a porcelain crucible, and weigh as magnesium pyrophosphate.

The precipitation of the metals present with hydrogen sulphide may be omitted and the separation effected by precipitating the phosphoric acid as molybdate. The dry residue should then be dissolved in nitric acid, and after filtering off the silica, the phosphoric acid is precipitated as directed in Chapter IX, page 118.

ANALYSIS OF MINERALS.

CHAPTER XIII.

MINERALS CONTAINING IRON, ALUMINIUM, AND CHROMIUM.

SELECTION AND PREPARATION OF SAMPLE.

205. Taking the Sample for Analysis.—One of the most important operations preliminary to many chemical analyses is the selection of the sample to be analyzed. When the material to be analyzed is a chemical, such as the various salts made for commercial purposes, the task is comparatively simple since the product is usually quite uniform and small grained. Samples are taken from a number of the barrels or other receptacles. In many cases it is advisable to take samples from various parts of the barrel, such as the end, middle, etc. This is most readily accomplished by means of a "butter-tryer" or "thief" or some similar apparatus. These various samples are brought together, thoroughly mixed, and a smaller sample taken out. This may be done by taking small portions from various parts of the pile or by dividing it into quarters. One quarter or two diagonal quarters are taken, well mixed, and the sampling repeated in the same manner until a convenient quantity for analysis is obtained.

Care in sampling dry and apparently uniform products is necessary for a good many reasons. Many substances when exposed to the air, as in the outer portions of a barrel, absorb or lose moisture, oxidize, lose volatile constituents, or in other ways change in composition. Even in the case of a mixture of two solid substances of different specific gravity the heavier constituent tends to settle to the bottom, so that after the most thorough mixing the material will not be uniform after standing for some time.

If LIQUIDS are to be sampled they must be thoroughly shaken or parts of the first, middle, and last runnings of a cask or drum

must be taken. These portions should be thoroughly mixed before taking the sample for analysis.

METALS and ALLOYS are by no means uniform, since, on solidifying from the molten state, the heavier constituents are apt to settle to the bottom, as do also the constituents which crystallize out or solidify first. In the case of a bar the outer portions are not always of the same composition as the interior of the metal. Drilling through a piece of metal with a clean tool is therefore apt to give the best sample. If the metal is in the form of a sheet, portions should be punched or cut from the outer edges as well as from the centre. If car-loads of metals as "*pigs*" are to be sampled, one or more "*pigs*" in each car should be punched or drilled and the samples combined by melting or mixing before the laboratory sample is taken. The turnings of the more brittle metals may be pulverized by grinding in a mortar or a coffee-mill.

If a ROCK is to be analyzed, the sample is usually selected because of its apparent homogeneity. The physical properties usually give sufficient evidence of the presence of foreign material. If the rock or mineral is to be analyzed with a view to its use as the source of a given metal or other constituent, the sample must include all foreign material which would be taken out in mining operations.

The cars or shiploads of ORE are usually sampled by taking out shovelfuls of the material from various parts of the load. These portions are thrown together on a floor or other convenient place. The larger pieces are broken with a hammer and the material well mixed. The pile is quartered and the quarter taken is still further powdered and quartered. This process is continued until a sample of convenient size is obtained. About 25 grams will usually be found sufficient, though in some cases as much as a kilogram will be required for the determination of elements present in very small amount.

206. Pulverizing.—The tools used in breaking off and powdering ores or rocks include, in the first place, HAMMERS with hardened surfaces. These are made in various shapes and sizes to suit the geologist prospecting in the field or the laboratory assistant in breaking up the large specimens of rock. A chilled IRON PLATE with a hardened steel MULLER to which a rocking

motion may be given by means of a long handle may be used to reduce many ores and rocks to powder fine enough for analysis.

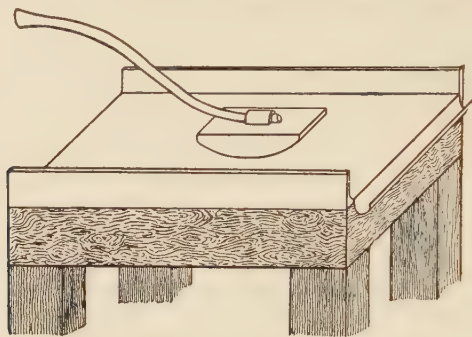


FIG. 21.

HARDENED STEEL MORTARS are also useful in crushing moderately small pieces of ore or rock. The most convenient method of

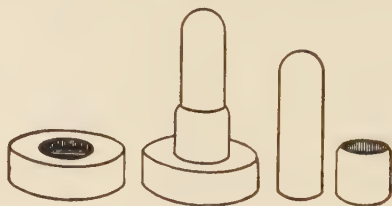


FIG. 22.

crushing large samples of rock or ore is by the use of ORE-CRUSHERS. The jaws between which the ore is placed are actuated by means

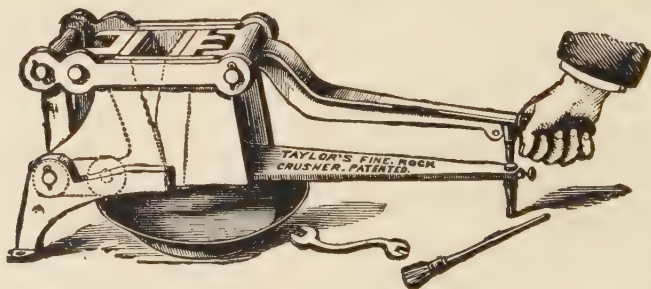


FIG. 23.

of a long handle so connected with levers that a very great crushing pressure may be brought to bear on the material. It is customary to remove by means of a magnet particles of iron which

have been detached from the tools during the process of pulverizing. Very few rocks or ores are entirely free from magnetic particles, so that this method of procedure is open to objection.

Hard rocks and ores, as well as those known to contain iron, should be pulverized as far as possible in AGATE MORTARS. These, as well as the iron mortars, are frequently arranged to be operated by mechanical means. Many chemists, however, still prefer the hand grinding.

207. Sifting.—The requisite degree of fineness is frequently secured by passing the powdered material through sieves of the requisite size of mesh. Eighty-mesh BRASS SIEVES are suitable for most ores. In special cases where the sample is very irregular, sieves of 100 to 120 mesh to the square inch should be used. Even when kept scrupulously clean a small amount of the metal of the sieve is apt to contaminate the sifted material. This error may be entirely disregarded if a constituent present in very small amount is to be determined. When a complete analysis is to be made, many chemists prefer to use BOLTING-CLOTH or FINE LINEN. Where the state of oxidation of the iron is to be determined, the shreds of the cloth, which almost necessarily contaminate the sifted material, undoubtedly influence the result to an appreciable degree. For this reason some chemists advocate grinding the material without sifting at all.

In sifting through cloth large particles are readily forced through if the powder is rubbed over the cloth. A wide-mouthed bottle should be selected, thoroughly cleaned and dried. The cloth should be stretched over the mouth of the bottle and fastened securely by winding a string around the neck. The material to be sifted, after having been ground in small portions in an agate mortar, is placed on the cloth and a piece of sheet rubber or leather stretched over the mouth of the bottle and held securely with the hand or by a rubber band placed around the neck. The rubber or leather is now lightly tapped with a spatula until no more fine material sifts into the bottle. The coarser material is again ground in the mortar and sifted. In no case should the coarse material be discarded. Frequently the more friable portions of a rock or ore are different in composition from the particles which resist grinding longest. In pul-

verizing a sample the rule must be strictly adhered to that *the whole of a portion taken for powdering must be ground and passed through the sieve*. In sampling, the large pieces must be broken completely so as to mingle with the finer material and constitute a fair portion of the sample finally taken.

208. Drying.—After being reduced to a sufficient state of fineness, the material to be analyzed is frequently dried at a temperature of about 100° to remove hygroscopic moisture before being weighed out. Other workers weigh out the air-dried material and determine the percentage of water lost at 100° . It is held that the amount of hygroscopic water present is a very characteristic property of some rocks and minerals, and serves to distinguish minerals which are in other respects identical. Hygroscopic material can also be weighed out much more accurately when air-dried than when entirely desiccated. In the latter case it gradually absorbs moisture, as it is exposed to the air from time to time in the course of the analysis, so that the material weighed out the first day is not identical in composition with that weighed out later.

SEPARATION OF IRON, ALUMINIUM, AND CHROMIUM.

Iron and aluminium occur very frequently together, and are generally precipitated together from solutions containing manganese, cobalt, nickel, and zinc. The methods suitable for precipitating these two metals are not generally applicable to the complete precipitation of chromium. The separation of iron and aluminium will therefore be first considered, and then that of chromium.

209. Separation as Hydroxide.—In the presence of excess of ammonium chloride and ammonia, nickel, cobalt, and zinc are not at all, while manganese is only slowly precipitated by being oxidized to the hydrated sesquioxide, while ferric iron, aluminium and chromium are very nearly completely precipitated. If all of these metals are present in solution, the iron, aluminium, and chromium may be completely precipitated by means of ammonia and ammonium chloride, but the precipitate will be contaminated with considerable amounts of manganese and varying amounts of zinc, nickel, and cobalt. In the absence of chromium, by

redissolving and reprecipitating the iron and aluminium once or twice, the separation from nickel and cobalt may be made complete and very nearly so from zinc.

Only a small part of the other metals present in the solution will be carried down each time with the iron and aluminium precipitate. On dissolving the first precipitate only this small part of the contaminating metals will be present in the solution; the bulk of these metals will be in the filtrate. On making a second precipitation the fraction carried down will be very small indeed, so that on a third precipitation the amount carried down may be wholly neglected. This process will not free the precipitate from manganese, because this metal is oxidized very readily in alkaline solution to the insoluble dioxide.

The solution should be heated, excess of ammonia added, and if aluminium is present ammonium carbonate added. After digesting hot for some time the precipitate is filtered off, washed a few times, redissolved in hydrochloric acid, and the operation repeated. If the amount of nickel and cobalt is considerable, a third precipitation is necessary. Manganese must be absent. The precipitate may be ignited and weighed, and one of the constituents determined, the other one being obtained by difference.

210. Separation as Basic Acetates.—If manganese and zinc are present, the aluminium and iron must be precipitated as basic acetates. This method of separation is based on the fact that iron and aluminium may be precipitated as basic acetates by boiling a solution of these metals which contains ammonium or sodium acetate and free acetic acid. The acid present prevents the precipitation of manganese, zinc, cobalt, and nickel. The separation is therefore much sharper than when the iron and aluminium are precipitated from alkaline solution. Oxidizing agents must be absent or manganese will be precipitated, but the iron must be in the ferric condition.

The proportion of free acetic acid to ammonium acetate must be carefully regulated. They should be present in *gram-molecular proportion*. As the commercial ammonium acetate is not always neutral it should be tested before use and neutralized. The simplest way of securing the proper proportion of free acid and neu-

tral salt is to make the ammonium acetate by neutralization of acetic acid. If the same volume of acetic acid is neutralized as has already been added to the solution the correct amount of ammonium acetate will be secured. The volume of the solution must also be carefully regulated with reference to the amount of iron present.

The perfectly cold hydrochloric acid solution must be made very nearly neutral by the addition of concentrated and then dilute ammonium carbonate solution until the slightest turbidity is noticed. If a precipitate forms it must be dissolved in hydrochloric acid, and the solution again cautiously neutralized. One c.c. of 5 N acetic acid is added for each 0.1 gram of iron. Water is added until at least 150 c.c. is present for each 0.1 gram of iron. Heat to boiling in a porcelain dish, and add 1 c.c. of 5 N acetic acid which has been exactly neutralized with ammonia for each 0.1 gram of iron present. Continue the boiling for two or three minutes. After allowing the precipitate to settle, decant the liquid and wash by decantation a few times, bringing the wash-water to a boil each time before decantation. The precipitate is free from zinc and all but a trace of manganese, but if nickel and cobalt are present it is apt to contain a little of these metals, more of the former than of the latter. It may be freed from these metals by redissolving and reprecipitating. If the filtrate has a slight yellow color the iron has not been completely precipitated because of the presence of too much acetic acid. A few drops of ammonia may be added and the solution warmed until the precipitate collects. It is washed with hot water containing a little acetic acid and ammonium acetate.

This method gives better results with iron than with aluminium, unless iron is also present in considerable amount. Small amounts of chromium may also be precipitated by this method if considerable iron is present. The precipitate cannot be ignited and weighed if alkalis were present in the solution because it carries down alkalis which cannot be washed out. It must be dissolved in hydrochloric acid and reprecipitated with ammonia.

The method has the disadvantage that the precipitate is very bulky, and is frequently slimy and difficult to wash. For this reason it is not used when a large amount of iron must be handled.

211. Separation of Iron and Aluminium as Basic Carbonates.—

Iron and aluminium may also be separated from manganese, cobalt, nickel, and zinc, by precipitation of the former as basic carbonates. The hydrochloric acid solution is carefully neutralized with ammonium carbonate, until a slight turbidity appears. A drop or two of acetic acid is added. Ammonium chloride must be present to the extent of about 1 gram for each 0.1 gram of iron. The solution is gradually brought to a boil and the heating continued until the carbon dioxide is completely expelled. The precipitate is washed by decantation, a few drops of ammonia being added to the wash-water. A slight yellow color in the filtrate indicates incomplete precipitation of iron. A few drops of ammonia may be added, but care must be taken not to make the solution alkaline or manganese will be precipitated.

212. Separation of Chromium as Chromic Acid.—Chromium is best separated from other metals by methods which are based on the acid properties of chromium trioxide. It is converted into the acid oxide by treatment with an alkaline oxidizing agent. A mixture of sodium carbonate and potassium nitrate has been largely used for this purpose. On extracting the fused mass with water the oxides of zinc, cobalt, nickel, and iron remain undissolved. Part of the manganese remains undissolved while part goes into solution as manganate. On boiling the solution after the addition of a little alcohol the manganese is completely precipitated as the dioxide. Part of the aluminium remains with the insoluble portion, while part passes into solution with the sodium chromate as sodium aluminate. The aluminium may be separated from the chromium by precipitation as aluminium hydroxide. The solution must be acidified with hydrochloric acid to decompose the sodium aluminate. On adding ammonium chloride and ammonia until the solution is faintly alkaline and warming, the aluminium is completely precipitated as hydroxide. The chromium in the condition of chromic acid is not precipitated by the ammonia.

The potassium nitrate used to oxidize the chromium is reduced during the fusion to nitrite which is present in the water solution of the melt. On acidifying this solution, nitrous acid is liberated which tends to reduce the chromic acid. To destroy the nitrous

acid potassium chlorate or still better liquid bromine is added to the alkaline solution. On acidifying and warming gently, the nitrous acid is oxidized and the excess of bromine or chlorine expelled. The chromium in the filtrate from the aluminium may be precipitated and weighed as lead or barium chromate. It may also be reduced by sulphurous acid, precipitated with ammonia and weighed as oxide, or it may be determined volumetrically by means of ferrous sulphate and a standard chromate solution.

Recently fusion with SODIUM PEROXIDE has come into extensive use. This flux seems to be especially adapted to decompose the refractory chrome iron ore. A silver, nickel, or copper crucible must be used, as platinum is strongly attacked by the alkaline flux. A mixture of 5 to 6 parts of caustic soda with 3 to 4 parts of sodium peroxide has also been considerably used.

If the chromium is in solution with other metals the separation is not so simple. The acid solution is nearly neutralized with sodium carbonate, sodium acetate added, the solution heated, and chlorine passed or bromine added. The chromium is oxidized to chromic acid and remains in solution. Iron and aluminium are precipitated during the boiling by the sodium acetate. Any manganese present is precipitated as the peroxide together with part of the cobalt, nickel, and zinc.

213. Rothe's Ether Separation of Iron.—The method proposed by J. W. Rothe for the separation of iron from *chromium, aluminium, manganese, cobalt, nickel, and copper* has been much used, and overcomes many difficulties met with in analyzing compounds containing much iron. It depends on the fact that ferric chloride may be almost completely extracted by means of ether from a hydrochloric acid solution of sp. gr. 1.100 to 1.105 containing the metals mentioned. Nitric acid, chlorine, and more than small amounts of sulphuric acid must be absent, and the solution must be kept absolutely cold, as in a warm solution the ferric chloride is reduced by the ether. All suspended matter such as silica, carbon, etc., must be removed by filtration. The apparatus designed for this separation is shown in Fig. 24. The two bulbs *A* and *B* are connected by a three-way stop-cock at *E*, so that liquid may flow from one bulb to the other or from either bulb through the exit-tube to a receptacle placed below. If the

hydrochloric acid solution of the iron is placed in *A*, about an equal volume of ether is placed in *B*. A slight pressure is produced over the ether by means of a rubber bulb. By cautiously turning the stop-cock *E* into the position 2, the ether is allowed to flow into the bulb *A*. The liquids are well mixed by vigorous

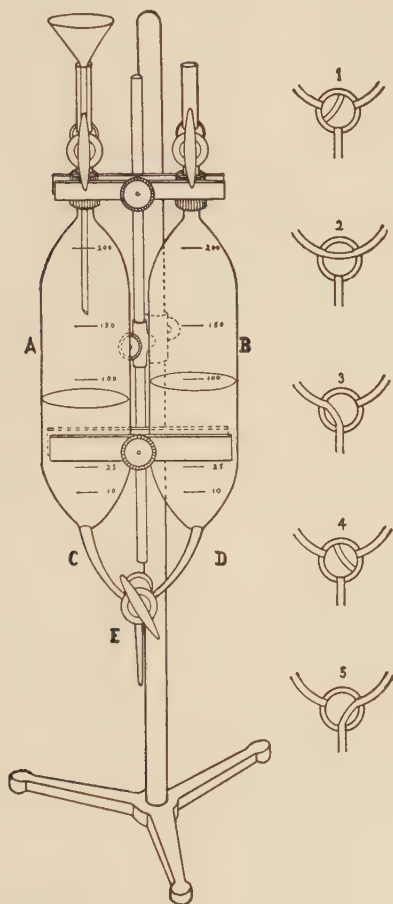


FIG. 24.

shaking. During this operation it is well to keep the bulb *A* well cooled by holding it in a stream of cold water. After allowing a few minutes for the liquids to separate, the stop-cock *E* is turned so that the lower heavy liquid may flow into *B*. Leave just enough of

this liquid to fill the capillary tube *C*, shake down any heavy liquid adhering to the sides of *A*, and allow to stand until the ethereal layer is clear. Again connect *A* and *B* by turning the stop-cock *C*, and transfer the remainder of the heavy liquid to *B* together with a little of the ether solution. Turn the stop-cock *E* into the position 3, and allow the ether solution to flow out into a beaker. Rinse the walls of the bulb *A* with a little ether, and after standing a few minutes observe if any of the heavy solution collects in *C*. If so, transfer as before to *B*. Repeat the extraction with 50 c.c. of ether. (See Exercise 35, page 170.)

214. Volumetric Separation of Iron and Aluminium.—The iron and aluminium precipitate obtained in separations from other metals is best ignited and weighed as $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ and one of the metals determined, the other being obtained by difference. For this purpose it is simplest to determine the iron volumetrically. The precipitate is fused with acid potassium sulphate until dissolved, the fused mass dissolved in water, and the solution filtered to separate a small amount of silica which may be present. This is ignited and weighed, and the amount deducted from the weight of the oxides. The solution of the iron and aluminium is treated with zinc to reduce the iron, which is titrated with standard potassium permanganate solution as directed in Chapter XXIV, page 316. If the precipitate is large it may be dissolved in hydrochloric acid before weighing and divided into two portions. The iron is determined in one portion while in the other both metals are precipitated as hydroxides, ignited, and weighed as oxides.

215. Separation of Iron from Aluminium as Aluminate.—The two metals may also be separated by means of boiling caustic potash or soda solution. The hydrochloric acid or potassium bisulphate solution of the two metals is nearly neutralized, and poured slowly with constant stirring into excess of caustic potash or soda solution, heated nearly to boiling in a platinum or silver dish. The iron is precipitated as hydroxide, while the aluminium remains in solution. The iron precipitate is washed more readily if part of it is reduced by adding a little sodium sulphite and heating before pouring into the boiling alkaline solution. Before weighing, the iron precipitate must be dissolved in hydrochloric acid and re-

precipitated with ammonia to free it from the alkali which is always present.

The aluminium in the filtrate is precipitated by acidifying with hydrochloric acid and just neutralizing with ammonia and warming. The caustic potash or soda must be free from impurities which are precipitated by ammonia and ammonium chloride. If pure caustic cannot be obtained by solution of the metal in water in a platinum or silver dish or other method, a blank determination of the amount of impurities present must be made.

EXERCISE 34.

Analysis of Chromite (FeO, MgO)($\text{Cr}_2\text{O}_3, \text{Al}_2\text{O}_3$).

Silica and Small Amounts of Manganese are Generally Present.

This ore is chiefly of value for its content of chromium. The determination of the amount of this element is the most important and frequently the only determination required. For this reason, and also for convenience in determining the amount of the other elements present, a separate portion is taken for the determination of chromium.

216. Solution of Ore.—Weigh one-half gram of the finely pulverized ore and mix in a small copper or nickel crucible with 2 to 5 grams of powdered sodium peroxide. Brush off carefully the platinum or glass rod used for mixing the material. If the sodium peroxide is not pure yellow and fresh, the larger amount should be taken, as it decomposes rapidly, forming sodium carbonate. Heat the crucible with a small flame of the Bunsen burner, so that the contents are completely fused only after several minutes. Keep the material fused for about ten minutes.

When cold, place the crucible in a porcelain dish and dissolve the contents in 50 to 100 c.c. of hot water. Boil for fifteen to twenty minutes to decompose the sodium peroxide.

217. Chromium.—Filter off and wash the precipitate consisting of iron, magnesium, manganese and some of the silica, as well as a little nickel or copper from the crucible. The filtrate will contain all of the chromium and aluminium and part of the silica. Acidify the filtrate with acetic acid, warm and filter off any alumina and silica which separates out. Precipitate the chromic acid by adding lead acetate or barium chloride and weigh as lead or barium chromate. The chromium may also be determined volumetrically as directed in Exercise 63, page 333. This volumetric method will usually be found superior to the gravimetric method.

218. Iron.—The insoluble material filtered off from the solution of the sodium peroxide fusion may be used for the determination of iron. It is dissolved in a little sulphuric acid, the material adhering to the crucible

being dissolved in the same manner. Particles of *undecomposed chromite* may be distinguished from the gelatinous silicic acid as a fine heavy powder which quickly settles to the bottom of the beaker on stirring the solution. If material of this kind is present it must be filtered off and again fused with sodium peroxide. The solution of the melt must be filtered and the filtrate added to the bulk of the chromium solution. The insoluble residue is dissolved in hydrochloric acid and added to the solution of the insoluble material from the first fusion. The iron may then be titrated as directed in Exercise 57, page 320.

219. Silica.—For the determination of the elements present other than chromium, a separate portion of one-half to one gram is fused with sodium peroxide, in the same manner as directed for the determination of chromium. The fused mass is dissolved in water, boiled to decompose the sodium peroxide and the insoluble matter filtered off and washed free from chromium. The filtrate is acidified with hydrochloric acid, evaporated to dryness and heated one-half hour on the water-bath to dehydrate the silicic acid, which is filtrated off and washed.

220. Aluminium.—The filtrate will contain the aluminium and the chromium. It is neutralized with ammonium carbonate and a little hydrogen peroxide or bromine added, and the solution boiled to reoxidize the chromium which has been reduced during the evaporation with hydrochloric acid. The solution should be boiled in a porcelain or platinum dish to avoid solution of the glass of the beaker in the alkaline liquid. The aluminium hydroxide is filtered off, washed free from chromium, ignited, and weighed as oxide.

The chromium and aluminium may also be precipitated together and weighed as oxides, the amount of aluminium being found by deducting the weight of chromium oxide as obtained by the previous determination of this element. The filtrate from the silica is warmed after the addition of alcohol or sulphurous acid to completely reduce the chromium. The aluminium and chromium are then precipitated with ammonia and weighed as oxides.

221. Silica.—The material insoluble in the sodium peroxide solution, which contains the manganese, magnesium, and part of the silica, is dissolved in warm hydrochloric acid and any undecomposed chromite filtered off and again fused with sodium peroxide. The acid solution of the insoluble matter is evaporated to dryness on the water-bath to dehydrate the silica which is filtered off, washed, and weighed, the weight being added to that of the silica already found, unless the same filter-paper was used for both precipitates.

222. Manganese.—If a copper crucible was used, hydrogen sulphide is passed through the acid filtrate from the silica to precipitate the copper dissolved, which is filtered off and washed. Bromine water or liquid bromine dissolved in hydrochloric acid is added to the filtrate to oxidize the iron and to decompose the excess of hydrogen sulphide. Sufficient bromine is added

to color the solution distinctly. Ammonia is added until the reaction is distinctly alkaline. The solution is warmed and the precipitate consisting of the iron and any manganese which may be present is filtered off and washed. It may be ignited and weighed, the manganese being obtained by difference, the amount of iron being known. The manganese will be present as Mn_2O_3 . If the amount of manganese is small it may be determined more accurately by Ford's method. The precipitate is dissolved in a little nitric acid and the determination carried out as directed in Chapter XXVIII, page 385.

223. The **magnesium** will be found in the filtrate from the iron precipitate. It is evaporated to small bulk, precipitated as magnesium ammonium phosphate, and weighed as pyrophosphate.

CHAPTER XIV.

ANALYSIS OF SULPHIDES CONTAINING MANGANESE, NICKEL, COBALT, AND MERCURY.

SEPARATION OF MANGANESE, NICKEL, AND COBALT.

224. Separation of Nickel and Cobalt as Sulphides.—One of the best methods of separating manganese from nickel and cobalt depends on the properties of the sulphides of these metals. The sulphide of manganese is readily soluble in dilute acids, including acetic acid. The sulphides of nickel and cobalt after precipitation are almost insoluble in all dilute acids. These two metals are not precipitated, however, from solutions acid with mineral acids, but do come down from warm acetic-acid solution.

The acid solution of manganese, cobalt, and nickel from which zinc, iron, aluminium, etc., have been separated by methods already given, is concentrated to a small bulk (30 to 50 c.c.). The solution is made alkaline with sodium carbonate, acidified with acetic acid and 3 to 4 grams of sodium acetate dissolved in a little water are added. The solution is heated to 70°, and hydrogen sulphide passed until saturated. The sulphides of nickel and cobalt are filtered off and washed. The filtrate and washings are concentrated, a little ammonium sulphide and then acetic acid are added, and hydrogen sulphide again passed. A little more of the cobalt and nickel sulphides is frequently obtained. A second test of the filtrate in this manner sometimes yields a small precipitate.

Another method of carrying out this separation which requires but one precipitation is as follows: The sulphate solution of manganese, cobalt, and nickel is transferred to a pressure-bottle of about one-half liter capacity. The solution is neutralized with ammonia, 30 c.c. ammonium-acetate solution (1 to 10), and 20 c.c. 50% acetic acid added. The solution is diluted to 300 to 400 c.c., and hydrogen sulphide passed for one to two hours. The bottle is closed, placed in a water-bath containing cold water which is

brought to a boil in one hour. The bottle is allowed to cool in the water-bath to 50°. The precipitated sulphides are filtered off and washed with water containing acetic acid and hydrogen sulphide.

225. Electrolytic Separation of Manganese from Cobalt and Nickel.—Small amounts of manganese can readily be separated from cobalt and nickel electrolytically. The sulphate solution of the three metals should be treated with 30 c.c. of a cold-saturated ammonium-sulphate solution, and 30 to 50 c.c. of ammonia (sp. gr. 0.96). The solution is diluted to about 150 c.c., and electrolyzed with a current of about 0.7 ampere at the ordinary temperature. The manganese separates as dioxide on the anode. This precipitate carries down small amounts of nickel and cobalt unless these metals are deposited before the manganese dioxide forms. Small amounts of nitrates and chlorides hinder the precipitation of nickel and cobalt. The deposited metal is washed with water without interrupting the current. Finally it is washed with alcohol, dried in the air-bath, and weighed.

SEPARATION OF NICKEL AND COBALT.

226. Precipitation of Cobalt as Tripotassium Cobaltic Nitrite, $\text{Co}(\text{NO}_2)_3 \cdot 3\text{KNO}_2$, separates it from nickel as well as from manganese and zinc. The alkaline earth-metals and iron must be absent. The method is satisfactory for mixtures of nickel and cobalt in all proportions, but is especially suited for the separation of a little cobalt from much nickel. The solution of the metals is evaporated to small bulk, and neutralized with potassium hydroxide. About 5 grams of potassium nitrite dissolved in water are added. Acetic acid is added until the solution is acid and nitrous fumes are evolved. It is allowed to stand for at least twenty-four hours. A portion of the supernatant liquid is taken out and tested for cobalt by adding more potassium nitrite. If a precipitate forms after long standing, more potassium nitrite must be added to the main solution. The precipitate is filtered off and washed with a solution of potassium acetate (1 to 10) containing a little potassium nitrite. The precipitate may be dissolved in hydrochloric acid and the cobalt reprecipitated with caustic soda

and weighed as oxide. It may also be dissolved in dilute sulphuric acid and the solution evaporated to dryness in a weighed platinum dish or crucible. The residue consisting of the sulphates of cobalt and potassium is heated to dull redness and weighed. If weighed in this manner the potassium acetate and nitrite must finally be washed out with a little distilled water. The precipitate may also be dissolved in hot dilute sulphuric acid, the solution concentrated, treated with excess of ammonia, ammonium sulphate added, and the cobalt determined electrolytically.

If the NICKEL has previously been weighed with the cobalt, it may be obtained by difference. Otherwise the nickel may be determined in the filtrate from the cobalt. For this purpose the solution is treated with hydrochloric acid and the nickel precipitated with caustic soda and bromine water. The nickelic hydroxide may be filtered off, washed, and reduced to metallic nickel by heating in a stream of hydrogen, or it may be dissolved in sulphuric acid and a little sulphurous acid and determined electrolytically.

227. Separation of Cobalt and Nickel by Means of Nitroso- β -Naphthol. — The cobalt compound $\text{Co}(\text{C}_{10}\text{H}_6\text{O}(\text{NO}))_3$ is insoluble in hydrochloric acid, while the corresponding nickel compound is soluble. Nitric acid is expelled by evaporation with sulphuric acid. The solution is diluted, 5 c.c. hydrochloric acid and a freshly prepared hot solution of nitroso- β -naphthol in 50% acetic acid added, until further addition produces no precipitate. The solution is digested in a warm place for a few hours. The precipitate, consisting of cobalt nitroso- β -naphthol as well as considerable of the reagent, is filtered off and washed, first with cold and then with warm 12% hydrochloric acid until all the nickel has been washed out. It is then washed with hot water until free from acid. The precipitate is dried and placed in a weighed Rose crucible. A little pure recrystallized oxalic acid is added and the paper burned, at first with low heat and then with the full flame of the Bunsen burner. When the carbon is completely burned the precipitate is reduced to metallic cobalt by heating in a stream of hydrogen.

The filtrate is evaporated after the addition of sulphuric acid. The NICKEL may then be precipitated as hydroxide and weighed as oxide, or it may be determined electrolytically.

EXERCISE 35.

Analysis of Smaltite (Co,Ni,Fe)(S,As).

Silica and Small Amounts of Manganese Are Usually Present.

228. Solution.—One gram of the finely powdered material is weighed out and transferred to an Erlenmeyer flask of about 250 c.c. capacity. This is best done by means of a small tube sealed at one end. The tube containing about one gram of the smaltite is carefully weighed. It is then inserted into the neck of the flask which is tilted. On raising the flask upright and tapping the tube gently the smaltite is deposited on the bottom of the flask. The tube is carefully withdrawn and weighed. Twenty c.c. of aqua regia, made by adding to 3 volumes of concentrated nitric acid 1 volume of concentrated hydrochloric acid, are added. A small funnel is placed in the neck of the flask and, after being shaken and standing until the violent action has ceased, the flask is warmed gently on the water-bath until the mineral is entirely decomposed. If sulphur floats on top of the solution, liquid bromine should be added, a few drops at a time, and the solution warmed until the sulphur is entirely oxidized.

229. Silica.—The solution is poured into a porcelain dish, the flask and funnel rinsed with water and after the addition of concentrated sulphuric acid, evaporated on the hot plate until fumes of sulphuric acid are copiously evolved. The solution is cooled and diluted with water. The siliceous residue is immediately filtered off, washed, and weighed.

230. Arsenic, Antimony, and Tin.—A little sulphur dioxide is added to the filtrate, which is warmed to reduce arsenic to arsenous acid. The excess of sulphur dioxide is expelled by boiling. Hydrogen sulphide is passed through the warm solution until no more precipitate forms. The arsenious sulphide is filtered off on a Gooch crucible and the filtrate again treated with sulphur dioxide and hydrogen sulphide to insure complete precipitation of the arsenic. After washing the arsenious sulphide the sulphur is extracted by treatment with alcohol and carbon disulphide. The precipitate is then dried and weighed. The color of the precipitate indicates the absence of lead, bismuth, and copper and all but a trace of antimony. The absence of the latter element as well as tin may be shown by treating the weighed precipitate with a concentrated solution of ammonium carbonate. The sulphides of antimony and tin remain on the filter and may be dissolved in hydrochloric acid and separated by the methods given in Chapter XI, page 134. The arsenic must also be reprecipitated and weighed.

231. Iron.—The filtrate from the hydrogen sulphide precipitate is evaporated with the addition of nitric acid to oxidize the iron. The solution is made alkaline with ammonia, warmed, and the precipitate filtered off

and washed two or three times. The filtrate will contain most of the cobalt and nickel, while the precipitate will contain all of the iron and a small amount of the nickel and cobalt. It is dissolved in dilute hydrochloric acid and the paper well washed. The solution is evaporated to a syrupy consistency and transferred with hydrochloric acid of sp. gr. 1.124 to the bulb *A* of the apparatus shown in Fig. 24, on p. 161, and the extraction with ether carried out as there described. The apparatus shown in Fig. 25 may also be used. Before transferring the solution to the bulb *D*, a few cubic centimeters of ether are poured into the bulb *D* and allowed to flow into *B*. By warming the bulb *B* with the hand and opening and closing the stop-cock *C*, a partial vacuum is created in *B*. *A* and *C* are closed and the solution transferred to *D*, rinsing the beaker with hydrochloric acid of sp. gr. 1.124 until the bulb is filled to the mark on *D*, making the volume 60 c.c. Place the bulb *B* in cold water, open the stop-cock *A*, and allow the liquid in *D* to flow into *B*. Close *A* and fill *D* with ether (100 c.c.) and allow it to flow slowly into *B*. Mix the liquids gradually, placing the bulb in cold water from time to time to prevent a large rise in temperature. Finally close *A*. Shake well, opening *A* occasionally to relieve the pressure, then place the apparatus in cold water for about five minutes to allow the liquids to separate.



FIG. 25.

Allow the lower liquid, which is very nearly free from iron, to flow into a beaker. Introduce about 10 c.c. of hydrochloric acid (sp. gr. 1.1) into the bulb *D*. Allow it to flow into *B*, shake, and after standing a few minutes allow the lower liquid to flow into the beaker. This liquid, together with the filtrate from the ferric hydroxide, will contain all of the cobalt, nickel, manganese, and aluminium and a little of the iron. Draw off the ether solution of the iron into another beaker and repeat the ether extraction of the iron, the nickel-cobalt solution being poured back again into the bulb *D*. Rinsing the beaker will be unnecessary.

The ether solution of the ferric chloride should be poured into a Florence or distilling flask connected with a condenser by means of cork stoppers and the beaker rinsed with water. The ether is distilled off on the water-bath, care being taken that the ether is not placed near a Bunsen burner or other flame. The ferric chloride is transferred to a beaker and the iron precipitated with ammonia and weighed as oxide, or reduced with zinc and determined volumetrically.

232. Aluminium and Chromium.— The combined cobalt nickel solution is warmed to expel the ether and a little bromine or hydrogen peroxide added. The solution is neutralized with ammonia, a little ammonium carbonate added, and boiled. A small precipitate of iron is usually obtained and any aluminium or chromium present is precipitated.

The precipitate, which is usually quite small, is filtered off, redissolved, and reprecipitated. In the absence of aluminium and chromium, it is added to the main portion of the iron and weighed. If aluminium and chromium are present, the metals must be separated by methods already given.

233. Manganese, Cobalt, and Nickel.—About 10 c.c. of concentrated sulphuric acid are added to the filtrate, which is evaporated on the hot plate until the hydrochloric acid is entirely expelled, as indicated by the evolution of dense fumes of sulphuric acid. After cooling, water is added and the solution is neutralized with ammonia. 30 to 50 c.c. of ammonia (sp. gr. 0.96) is then added and the nickel and cobalt determined electrolytically. The trace of manganese which may be present will be converted into the dioxide and deposited on the anode. It may be ignited and weighed as Mn_2O_4 .

The deposit of nickel and cobalt after being weighed is dissolved in warm dilute nitric acid and the solution evaporated to about 50 c.c. It is neutralized with caustic potash and 5 grams of potassium nitrite dissolved in water are added. Acetic acid is added until the solution is acid and the slight precipitate produced by the caustic potash dissolved. After standing for twenty-four hours, the clear liquid is tested for cobalt by adding more potassium nitrite. If cobalt is present, the entire solution must be allowed to stand for some time after the addition of potassium nitrite. The precipitate is filtered off and washed with a 10% solution of potassium acetate containing a little potassium nitrite. It is then dissolved in hot dilute sulphuric acid, excess of ammonia added, and the cobalt determined electrolytically.

234. Sulphur is determined in a separate portion of 0.5 gram, which is dissolved in aqua regia as already directed, or in fuming nitric acid. The reagents must be absolutely free from sulphur. If necessary, a blank determination should be made side by side with the determination of the mineral. Instead of the smaltite, a little pure sodium or potassium chloride should be added to the blank.

After the expulsion of the nitric acid with hydrochloric acid and filtering off the silica, the solution is ready for the precipitation of the sulphuric acid by means of barium chloride. If much sulphur is present, it is well to add a little sodium or potassium chloride to the nitric acid solution before evaporation to prevent loss of sulphuric acid. The evaporation should be conducted on a hot plate or water-bath which is wide enough to keep the products of combustion of the illuminating-gas away from the solution, otherwise sulphur dioxide may be absorbed. Sulphuretted hydrogen or ammonium sulphide must also be absent from the atmosphere.

The solution is diluted to 300 or 400 c.c., heated to boiling, and barium chloride solution added slowly with constant and vigorous stirring until no more precipitate forms on adding another drop of the reagent. After digesting the precipitate on the hot plate until the solution is clear, it is

filtered off, washed with hot water, ignited, and weighed. If the color of the ignited precipitate is not pure white, but reddish, iron has been carried down. Several grams of sodium carbonate are added to the precipitate and after fusion the melt is dissolved in water and the barium carbonate filtered off and washed. The sulphuric acid in the filtrate is precipitated by barium chloride after acidifying with hydrochloric acid. The error due to a *slight* reddish color of the precipitate may generally be neglected

EXERCISE 36.

Analysis of Pyrite, FeS_2 , Arsenopyrite, $\text{Fe}(\text{S}_2\text{As})_2$, or Chalcopyrite, CuFeS_2 .

Small Amounts of Silica, Arsenic, and Antimony May be Present.

235. Sulphur Available for Sulphuric-acid Manufacture.—As the natural sulphides are frequently used as a source of sulphur, especially in the manufacture of sulphuric acid, the determination of this element is frequently carried out for the purpose of ascertaining the amount of sulphur available under the conditions of manufacture of sulphuric acid. For this purpose the determination is carried out as follows:

One-half gram of the powdered sulphide is treated in an Erlenmeyer flask of about 250 c.c. capacity with 10 c.c. of a mixture of 3 volumes of concentrated nitric acid and 1 volume of concentrated hydrochloric acid. The mouth of the flask is closed with a small funnel and the solution is gently heated on the water-bath until the material is decomposed. If unoxidized sulphur separates, a few crystals of potassium chlorate are added from time to time and the heating continued until the globules of sulphur have disappeared. Liquid bromine may be added for the same purpose.

The solution is transferred to a porcelain dish and evaporated to dryness after the addition of one-half gram of pure sodium or potassium chloride. If the evaporation is conducted on the water-bath only, the addition of the alkali chlorides may be omitted. Five c.c. of concentrated hydrochloric acid are added and the solution again evaporated to dryness. The residue is dissolved in a few cubic centimeters of dilute hydrochloric acid and 100 c.c. of hot water. The insoluble residue is filtered off on a small paper and well washed with hot water. This residue consists of *silica, undecomposed silicates*, and the *sulphates* of *lead, barium, and calcium*, if these elements are present. This material is reserved for analysis to obtain the percentage of total sulphur present.

The filtrate is neutralized with ammonia and a considerable excess added. It is warmed for ten to fifteen minutes at $60^\circ\text{--}70^\circ$, but not to boiling. If the solution does not smell strongly of ammonia more must be added. The **FERRIC HYDROXIDE** is filtered off and washed twice by decantation with very hot water. The precipitate is transferred to the filter-paper, which should not be completely filled, so that it may be well stirred up with the stream of hot water. The precipitate must be washed until the wash-

water no longer gives a precipitate with barium chloride. As basic sulphates of iron may be present in the ferric hydroxide, the precipitate is dried and fused with sodium carbonate. The melt is dissolved in water and the solution tested for sulphuric acid.

The filtrate from the iron is acidified with hydrochloric acid, evaporated to a bulk of about 300 c.c., heated to boiling, and barium chloride solution added slowly with constant stirring until a considerable excess is present. Twenty c.c. of a 10% solution is usually more than sufficient for 0.5 gram of pyrite. After digesting hot until the solution is clear, the barium sulphate is filtered off, ignited, and weighed.

236. Total Sulphur.—To obtain the total percentage of sulphur the material insoluble in aqua regia is fused with sodium carbonate. If lead is absent, the fusion may be conducted in a platinum crucible, otherwise a porcelain crucible must be used. The melt is dissolved in hot water, filtered, the residue well washed, and the sulphuric acid in the filtrate precipitated with barium chloride and weighed.

The total percentage of sulphur may also be determined as follows: Fuse 0.5 gram of the sulphide with 10 grams of a mixture of two parts sodium carbonate and one part potassium nitrate. The material should be well mixed by stirring with a platinum or glass rod, which is then cleaned with a camel's-hair brush. The material is gradually brought to fusion and maintained in the fluid state for some time. The fused mass is extracted with hot water. If lead is present it is precipitated by passing carbon dioxide through the solution. The insoluble material is filtered off and washed with hot water containing a little sodium carbonate, first by decantation and then on the filter-paper.

The filtrate is acidified with hydrochloric acid and evaporated to dryness to remove nitric acid. The residue is dissolved in hot water to which a little hydrochloric acid has been added. Any insoluble material present is filtered off and well washed. The sulphuric acid in the filtrate is determined by precipitation with barium chloride.

237. Arsenic.—For the determination of ARSENIC, ANTIMONY, and COPPER, a portion weighing from 0.5 to 2 grams is taken. If the percentage of these elements is small, the larger amount is taken. The material is treated cold in a beaker with 20 to 30 c.c. concentrated hydrochloric acid. The solution is agitated from time to time. One or two c.c. of liquid bromine or concentrated nitric acid are then added and the solution is heated, gently at first and then more strongly, until the bromine or nitrous fumes are expelled. The arsenic is then distilled and determined as directed in Chapter XI, p. 133. Ferrous sulphate or chloride is used as the reducing-agent.

238. Antimony.—The contents of the flask are rinsed into a beaker, the solution diluted to 200 to 300 c.c., warmed, and hydrogen sulphide passed. The precipitate, consisting of the sulphides of copper and antimony, is filtered off and washed with water containing hydrogen sulphide. The

antimony sulphide is dissolved in a little sodium-sulphide solution and the residue washed with water containing a little sodium sulphide. The sodium sulphide may be made by saturating with hydrogen sulphide one-half of a caustic soda solution and then adding the other half. The antimony is precipitated by neutralizing the sodium sulphide solution with hydrochloric acid and passing hydrogen sulphide. It may be ignited and weighed as the tetroxide after treatment with nitric acid.

239. Copper.—The copper sulphide is dissolved in a little nitric acid and determined electrolytically.

240. Iron.—Iron is usually determined volumetrically. The ammonia precipitate from the aqua-regia solution made for determining sulphur contains nearly all of the iron. A small amount is frequently left in the insoluble residue as ferrous silicate. On fusing this residue with sodium carbonate the ferrous silicate is decomposed and the insoluble ferric hydrate may be filtered off. These two precipitates may be dissolved in hydrochloric acid and the iron titrated, as given in Chapter XXIV, page 320.

Both iron and silica may be determined in the portion fused with sodium carbonate and potassium nitrate for the determination of total sulphur. All of the iron will be present in the precipitate filtered off from the water solution of the fused material. It may be dissolved in hydrochloric acid, precipitated with ammonia and weighed as oxide, or it may be determined volumetrically.

241. Silica.—The silica constitutes the insoluble material filtered off after acidifying the sodium carbonate solution, evaporating to dryness and dissolving in hydrochloric acid and water. It is ignited and weighed.

EXERCISE 37.

Analysis of Cinnabar, HgS .

Iron, Manganese, Copper, Aluminium, and Calcium may also be Present.

Sulphur is determined by the method given on p. 167.

242. Mercury.—One gram of the mineral is treated with 20 to 30 c.c. concentrated hydrochloric acid to which 40 c.c. water is added. One to two grams of potassium chlorate are added in small portions and the solution warmed until the cinnabar is entirely decomposed. The solution is evaporated to dryness on the water-bath and the residue dissolved in water and hydrochloric acid. Any insoluble material is filtered off, ignited, and weighed. A little sulphurous acid is added to reduce any iron present to the ferrous condition. The solution is warmed to expel the excess of sulphurous acid and hydrogen sulphide passed until no more precipitate is formed. If copper is absent, the mercuric sulphide is filtered off on a Gooch crucible which has been dried at 100° . Sulphur is extracted by washing the precipitate with alcohol and carbon disulphide. The precipitate is then dried at 100° and weighed.

If copper is present the precipitate, after being washed, is dissolved in aqua regia and the chlorine expelled by boiling after the addition of dilute

hydrochloric acid. When entirely free from chlorine or nitric acid, phosphorous acid is added and the solution is allowed to stand in a warm place for at least twelve hours. The precipitated mercurous chloride is filtered off on a Gooch crucible, washed with hot water, dried at 100° , and weighed.

243. Copper.—The filtrate is evaporated to small bulk after the addition of a few cubic centimeters of dilute sulphuric acid to expel the hydrochloric acid, diluted with water, and the copper determined electrolytically. The copper may also be precipitated as sulphide which is dissolved in 2 or 3 c.c. of concentrated nitric acid, the solution diluted and electrolyzed.

244. Mercury may also be determined very accurately in a separate portion as follows: A combustion-tube 30 to 45 cm. long and 10 to 15 mm. wide is taken. The end is sealed, then a layer of magnesite in large pieces, chalk, or sodium bicarbonate is introduced until the tube is filled for about 10 cm. Then a layer of recently ignited lime is introduced, occupying about 5 cm., then an intimate mixture of the ore with lime for about 6 cm. This mixture should be made by grinding the constituents together in a mortar. The mortar should be rinsed with lime, which is next introduced, occupying about 5 cm. Finally a layer of about 5 cm. of lime is introduced, and a loose plug of asbestos inserted. The tube is then drawn out and bent at right angles. It is then tapped gently so as to produce a free passage for the gases the entire length of the tube, and is then placed in a combustion-furnace with the drawn-out end dipping into a flask.

The burners of the furnace are lighted so that the lime near the drawn-out end of the tube is first heated to redness. The burners are then lighted in order until the magnesite in the closed end of the tube evolves carbon dioxide, which sweeps out the last traces of mercury vapor. While the tube is still hot it is cut off at the point where it was drawn out and bent and the globules of mercury washed out of the portion cut off by means of a jet of water. By shaking the flask the mercury is brought together into a single drop. The water is decanted and the mercury transferred to a weighed porcelain crucible. The water is absorbed in filter-paper and the mercury dried in a desiccator and weighed.

245. The Iron, Aluminium, Manganese, and Calcium will be present in the filtrate from the mercuric sulphide. If the amount of iron and aluminium is small, these metals may be precipitated as hydroxides and weighed as oxides. The separation from manganese is effected in the manner described in Exercise 33, p. 149, except that an excess of ammonia must be avoided or the aluminium will be redissolved. The manganese is determined as directed in the same exercise. The filtrate from the manganese is acidified with hydrochloric acid and evaporated to a bulk of 200 or 300 c.c. It is neutralized with ammonia, warmed nearly to boiling, and a little ammonium oxalate added. After digesting for some time, the calcium oxalate is filtered off and washed with hot water. The moist precipitate is placed in the platinum crucible, the paper burned in the usual manner, and the precipitate ignited, finally, over the blast-lamp and weighed as oxide.

CHAPTER XV.

ANALYSIS OF CARBONATES CONTAINING CALCIUM, BARIUM, STRONTIUM, AND MAGNESIUM.

SEPARATION OF CALCIUM, BARIUM, AND STRONTIUM FROM THE ALKALI METALS AND FROM EACH OTHER.

246. Calcium, Barium, and Strontium may be separated from magnesium and the alkali metals by precipitation as carbonates, by ammonia and ammonium carbonate. A sufficient amount of ammonium salts must be present to prevent the precipitation of magnesium. It is very seldom that this method of separation is used because the occurrence of these three elements together is very rare, although recent work has shown that traces of barium and strontium occur in rocks far more frequently than was formerly supposed. Excellent methods of separation of each of the alkaline-earth metals from magnesium and the alkalies are available, by which the metal is left in the best condition for weighing.

SEPARATION OF CALCIUM.

247. Separation of Calcium as Oxalate.—Calcium is usually separated from magnesium and the alkali metals by means of ammonium oxalate. The precipitation is carried out in a hot solution. Sufficient ammonium oxalate must be present to convert both calcium and magnesium into oxalates, since calcium oxalate is slightly soluble in magnesium chloride. Enough ammonium chloride must be present to prevent the precipitation of magnesium hydroxide when the solution is made alkaline. A sufficient amount is usually present from the precipitation of iron and aluminium. If an excessive amount has been introduced, it must be removed by evaporating the solution to dryness and volatilizing the ammonium salts. The solution may also be boiled down to small bulk and the ammonium salts decomposed by the addition of nitric acid. It is generally sufficient to treat in this

manner the filtrate from the second, third, and subsequent precipitations of the iron and aluminium. If the ammonium salts from the entire solution have been expelled, the residue is dissolved in hydrochloric acid and the solution neutralized with ammonia. If a precipitate forms it is dissolved in acid, and the solution again neutralized. This is repeated until a precipitate of magnesium hydroxide is no longer formed on making the solution alkaline.

The first precipitate of calcium oxalate will invariably contain some *magnesium* and also some *sodium*, which cannot be washed out. It must therefore be redissolved in hydrochloric acid, and reprecipitated by neutralizing with ammonia and adding a little ammonium oxalate. The second precipitate will be free from magnesium and sodium. If STRONTIUM is present it will be almost completely precipitated with the calcium. The two metals may be weighed together as oxides after ignition of the oxalate, and separated by methods given later. If BARIUM is present to the extent of 3 or 4 mg., it will not contaminate the calcium after the second precipitation. If more than 3 or 4 mg. of barium are present, the calcium cannot be separated as oxalate.

248. Separation of Barium and Strontium as Sulphates.—Barium and strontium may be separated from magnesium and the alkali metals by precipitation as sulphate. If strontium is present an equal volume of alcohol must be added to insure complete precipitation. The precipitate must also be washed with alcohol. Barium sulphate frequently carries down a small amount of the alkalis which cannot be washed out. It must, therefore, in very exact analyses, be redissolved in a little warm concentrated sulphuric acid and reprecipitated by diluting with water.

249. Separation of Calcium as Sulphate.—Calcium may also be separated from magnesium and the alkalis by precipitation as the sulphate. The solution must be evaporated until free hydrochloric acid and water are expelled. The residue is dissolved in alcohol, and a slight excess of concentrated sulphuric acid added. After digesting for some time the solution is filtered and the precipitate is washed with absolute alcohol until free from acid. A small amount of magnesium sulphate is then washed out by means of 35 to 40% alcohol. The alcohol may be expelled from the filtrate and the magnesium precipitated as phosphate. If barium

and strontium are present they will be precipitated with the calcium.

SEPARATION OF BARIUM, STRONTIUM, AND CALCIUM.

250. Precipitation of Barium as Chromate.—Two absolutely reliable methods for the separation of barium, strontium, and calcium have been devised by Fresenius. The metals are precipitated as carbonates with ammonia and ammonium carbonate. If the separation from the magnesium has been effected by sulphuric acid the precipitate is fused with sodium carbonate, the melt treated with hot water, and the carbonates of the alkaline-earth metals filtered off and well washed. The precipitate is dissolved in the least amount of dilute hydrochloric acid, and the excess removed by evaporation. The chlorides are dissolved in 300 c.c. of water, 6 drops of acetic acid (sp. gr. 1.065) and a few drops of ammonium acetate added. The solution is heated, and 10 c.c. of a neutral 10% ammonium chromate solution added. After allowing the precipitate to settle and the solution to cool for one hour, decant on a small filter and wash by decantation two to three times with water containing ammonium chromate. Finally transfer the precipitate to the paper and wash until the filtrate gives no precipitate with ammonia and ammonium carbonate. About 100 c.c. of wash-water should be used. The washing is continued with pure warm water, until the filtrate gives only a slight reddish coloration with silver nitrate. About 110 c.c. will be required.

The precipitate which contains all of the barium and a little of the strontium is washed into the precipitating-dish, the portion adhering to the filter-paper dissolved in a little warm dilute nitric acid, and the paper well washed. About 2 c.c. nitric acid (sp. gr. 1.20) should be used. The solution is diluted to 200 c.c. and heated. 5 c.c. of a 30% ammonium acetate solution is added very gradually. Ammonium chromate solution (10%) is then added until the odor of acetic acid has entirely disappeared. After standing one hour, the supernatant liquid is decanted through the filter or on a Gooch crucible, and the precipitate is digested with hot water which is allowed to cool. The precipitate

is then brought on the filter-paper or crucible and washed with cold water until the filtrate gives a scarcely perceptible test for chromic acid with silver nitrate.

251. Weighing Barium as Chromate.—The now pure barium chromate is removed from the paper, the latter burned, and the whole gently ignited in a platinum or porcelain crucible. If the heat is too great the chromic acid will be reduced and the precipitate will become green. The portions of the precipitate adhering to the filter-paper will also be reduced during the incineration of the latter. On gently heating the precipitate, the chromium will be reoxidized. If a Gooch crucible has been used the precipitate may finally be washed with alcohol, dried on the hot plate, and weighed.

252. Separation of Calcium and Strontium as Nitrates.—One c.c. of nitric acid is added to the filtrate from the barium, which is concentrated and the calcium and strontium precipitated by ammonia and ammonium carbonate. If only strontium is present the precipitate of strontium carbonate may be weighed or it may be dissolved in hydrochloric acid, precipitated by the addition of sulphuric acid and alcohol, and weighed as sulphate. If only calcium is present the precipitation as carbonate may be omitted and the calcium immediately precipitated as oxalate and weighed as oxide.

If both strontium and calcium are present the mixed carbonates are dissolved in nitric acid and the solution evaporated to dryness in a small porcelain dish and heated for some time in an air-bath at 130° . The temperature may rise to 180° without decomposing the nitrates. The dried material is pulverized and treated five times with 5-c.c. portions of a mixture of equal parts of absolute alcohol and ether and the solution decanted each time into a small flask. The calcium nitrate is dissolved by the alcohol and ether in which the strontium nitrate is insoluble. After expelling the ether and alcohol from the residue, it is dissolved in water, evaporated to dryness, and again heated for some time at 130° in the air-bath. The mass is pulverized and transferred to the flask with about 15 c.c. of the ether-alcohol. The flask is corked and allowed to stand with occasional shaking for twenty-four hours. The solution is then filtered through a small filter, the strontium

nitrate washed by decantation and then on the filter with 5-c.c. portions of the ether-alcohol about ten or twelve times. The strontium nitrate in the flask, on the paper, and in the dish, if it was not all transferred, is then dissolved in a little hot water and the strontium precipitated as sulphate by the addition of sulphuric acid and alcohol. The calcium in the ether-alcohol solution may be precipitated as sulphate and washed with absolute alcohol. It is ignited at a low red heat and weighed as calcium sulphate. The ether and alcohol may also be distilled off, the calcium nitrate dissolved in water, and the calcium precipitated as oxalate and weighed as oxide.

As BARIUM as well as STRONTIUM nitrate is insoluble in the ether-alcohol mixture, the carbonates of the three metals may be converted into nitrates and treated in the manner directed for the separation of calcium and strontium. The nitrates of barium and strontium may then be dissolved in water and the barium separated from the strontium by two precipitations of the barium as chromate. Gooch and Browning have suggested the use of amyl alcohol in place of the mixture of absolute alcohol and ether. As the amyl alcohol boils at 138° , it may be rendered anhydrous by boiling out the water. The preparation of absolute alcohol or ether is quite laborious.

EXERCISE 38.

Analysis of Dolomite, $(\text{CaO}, \text{MgO})\text{CO}_2$.

Small Amounts of Silica, Iron, Aluminium, and Manganese Are Usually Present.

253. Solution of the Dolomite.—One gram of the powdered material is weighed out, placed in a beaker (about 100 c.c.), and dissolved in about 15 c.c. dilute hydrochloric acid. The beaker should be covered with a watch-crystal and the acid poured slowly down the lip to prevent loss by spattering. The beaker is warmed on the hot-plate or water-bath until carbon dioxide ceases to be evolved. The watch-crystal is rinsed with a little water and the open beaker heated on the water-bath until the solution is evaporated to a syrupy consistency. It is then stirred with a glass rod until dry. The residue is heated at least one-half hour on the water-bath and then dissolved in water and a little hydrochloric acid and the solution heated for a few minutes.

254. Silica.—The siliceous residue is filtered off on a small paper and washed with hot water until free from chlorides. The moist paper is placed in a weighed platinum crucible, burned in the usual manner, and the siliceous residue finally ignited for a few minutes over the blast-lamp and weighed. The silica is then volatilized by moistening the weighed precipitate with water, adding 2 or 3 c.c. of hydrofluoric acid and a drop of sulphuric acid, warming until the precipitate is dissolved, and then evaporating to dryness on the hot-plate and igniting. The hydrofluoric acid must leave no residue on evaporation. Finally the residue in the crucible is ignited over the blast-lamp and brought to constant weight. The weight of the residue must be subtracted from the weight of the siliceous residue to obtain the weight of silica. The residue is dissolved in hydrochloric acid and added to the filtrate from the silica.

255. Iron and Aluminium.—Ten c.c. of concentrated hydrochloric acid are added to the acid solution, which should not exceed 200 c.c. It is neutralized with filtered ammonia while stirring vigorously and heated nearly to boiling on the hot-plate. If an excess of ammonia is present, very dilute hydrochloric acid is added until the faintest odor of ammonia can be detected over the hot solution or a moist piece of red litmus-paper held over the solution is slowly turned blue. The neutralization and digestion should not occupy more than one-half hour and a Jena beaker should be used. The precipitate of iron and aluminium is filtered off and if more than a few flakes are present, it is dissolved in a little warm dilute hydrochloric acid, the paper washed a few times with hot water, and the solution again neutralized with ammonia, digested on the hot-plate for a short time, and filtered. The precipitate is washed free from chlorides with hot water, the moist paper transferred to the platinum crucible and burned. The precipitate is heated with the blast-lamp for a few minutes and weighed. As this precipitate seldom weighs more than a few milligrams, the separation of the iron and aluminium is not necessary.

256. Manganese.—If the combined filtrates from the iron and aluminium exceed 300 c.c., the solution should be acidified with hydrochloric acid and concentrated on the hot-plate. To precipitate the manganese the solution is made alkaline with ammonia and bromine water or hydrogen peroxide is added. A few cubic centimeters of hydrogen peroxide are sufficient, while enough bromine water must be added to produce a yellow color in the solution. It is heated nearly to boiling, ammonia added if necessary to make it alkaline, the precipitate filtered off on a small paper and washed with hot water. The moist paper is burned in the crucible and the manganese weighed as Mn_2O_4 .

257. Calcium.—The filtrate is again concentrated on the hot-plate to about 250 c.c. after acidifying with hydrochloric acid. The calcium is precipitated by making the solution alkaline with ammonia and adding to the hot solution with vigorous stirring 30 to 40 c.c. of a 5% solution of

ammonium oxalate. The solution is digested on the water-bath for about one hour or until the precipitate has settled, leaving a clear supernatant liquid. This is decanted through a filter-paper and the precipitate in the beaker is washed two or three times by decantation with hot water. About 50 c.c. of water are used each time. The precipitate is well stirred up each time and allowed to settle. A little warm dilute hydrochloric acid is poured over the precipitate on the paper and allowed to flow into the beaker containing the main portion of the precipitate. The calcium is reprecipitated by neutralizing the hot solution with ammonia while stirring vigorously. A few cubic centimeters of ammonium oxalate are added and the precipitate digested on the hot-plate as before. Finally the calcium oxalate is filtered off and washed with hot water until free from chlorides. The moist precipitate may be placed in the platinum crucible, gently heated until dry, and the paper burned, then heated more strongly until the carbon is completely incinerated, and finally with the blast-lamp for five to ten minutes. After weighing, the heating with the blast-lamp and weighing are repeated until the weight is constant.

258. Magnesium.—The filtrates from the calcium are combined and, after acidifying with hydrochloric acid, evaporated on the hot-plate to 200 or 300 c.c. Excess of disodium phosphate or sodium ammonium phosphate solution and a moderate excess of ammonia are added with stirring. After being allowed to stand for twenty-four hours the solution is decanted quite completely from the precipitate, which is dissolved in a few cubic centimeters of dilute hydrochloric acid. A few drops of phosphate solution are added, then ammonia with stirring, until a moderate excess is present. The volume of the solution should now not be greater than 50 to 75 c.c. After standing from twelve to twenty-four hours, the precipitate is filtered off and washed with dilute ammonia until free from chlorides. It is then dried, detached from the paper, and the latter burned on the platinum wire. The precipitate may also be placed in the crucible followed by the folded paper. The precipitate is first heated gently, the lid being on the crucible. When ammonia is no longer evolved, the full flame of the Bunsen burner is applied and finally the blast-lamp for a few minutes.

259. Carbon Dioxide by Loss.—If the dolomite is free from organic matter, carbon dioxide may be determined by loss after fusing with borax.* For this purpose 5 grams of vitrified borax are fused in a platinum crucible with the Bunsen burner. If considerable water is present, it may be more quickly expelled by heating over the blast-lamp. As borax is slightly volatile at this temperature, the material must be brought to constant weight by heating to fusion with the Bunsen burner. One gram of the dolomite is placed on the borax, the lid is placed on the crucible, and the contents are

* Microcosmic salt may also be used for this determination, as described on page 111.

brought to fusion with the Bunsen burner. The lid must not be removed until the borax is fused, as it is apt to crack so that small pieces may be thrown out of the crucible. When the dolomite has dissolved in the melted borax and bubbles of gas escape only at considerable intervals, the crucible is cooled in the desiccator and weighed. When the weight is constant, the amount of carbon dioxide is found from the loss in weight of the borax and dolomite. The borax-glass may be removed from the crucible by pressing it between the thumb and fingers on all sides. This generally loosens the melt so that it drops out on gently tapping the crucible.

DIRECT WEIGHING OF CARBON DIOXIDE.

260. Apparatus.—Carbon dioxide may also be determined by absorption in caustic potash and ascertaining the increase in weight. For this purpose the apparatus shown in Fig. 18, p. 113, is very convenient and easily made. The glass tube is about 70 cm. long and not less than 12 mm. in diameter. It is drawn out so as to pass through the rubber stopper in the flask. The upper half is filled with granulated calcium chloride, a plug of asbestos or glass wool being first inserted and pushed to the middle of the tube. A few lumps of pumice-stone which have been saturated with copper sulphate solution and dried at about 125° are first dropped in to absorb any hydrochloric acid gas which may pass over. Large lumps of calcium chloride are then dropped in and then smaller ones, the fine material being at the end where another plug of cotton or glass wool is placed. After being filled in this manner, each end is connected with a calcium chloride tube or other drying apparatus and a slow stream of carbon dioxide or hydrochloric acid gas passed through the tube. This is maintained for twenty-four hours, when the acid gas is displaced by a stream of air. The upper end of the tube must be carefully protected from exposure to the atmosphere or moisture. The flask may have a capacity of 100 or 200 c.c. The end of the dropping-funnel should be drawn out and the end of the small tube turned up to prevent the escape of carbon dioxide through the dropping-funnel. A straight calcium chloride tube filled with soda-lime is fitted to the dropping-funnel by means of a small perforated rubber stopper.

261. For the **Geissler caustic potash bulb** a solution of caustic potash is made by dissolving one part of the potash in two parts of water. The bulbs are filled not more than two-thirds full with this solution. The calcium chloride tube is filled with soda-lime and calcium chloride, the soda-lime being nearest the caustic potash. The calcium chloride should be moderately fine, so that the gases may leave the apparatus well dried. Before placing the soda-lime in the tube a small plug of glass wool or cotton should be inserted. If a caustic potash bulb without the attached calcium chloride tube is used a separate U-tube or straight calcium chloride tube must be filled as directed and weighed separately.

262. Testing for Air Leaks.—When setting up the apparatus, it is well to shellac the small end of the rubber stoppers, as rubber is pervious to carbon dioxide. The small entrance-tube of the Geissler bulb can generally be inserted directly into the rubber stopper in the end of the glass tube, thus saving an extra rubber joint. When the apparatus has been set up, it is tested for leaks by closing the stop-cock in the dropping-funnel and sucking out a little air through the caustic potash bulb. Enough air should be sucked out to cause the solution to rise an inch or two in the limb of the Geissler bulb nearest the long glass tube. This column of liquid forms an index of the partial vacuum in the apparatus. The position of the liquid is carefully noted. If the liquid slowly falls, a leak exists which must be found and closed. The most delicate index is formed by the small drops of liquid that generally remain in one end of the small tubes connecting the bulbs of the absorption apparatus. If the apparatus is absolutely gas-tight, a drop of this kind will remain motionless for ten to fifteen minutes.

263. Determination of the Carbon Dioxide.—When the apparatus has been made tight, 1 gram of the dolomite is weighed out and transferred to the flask. After replacing the flask the apparatus is again tested for leaks. Air is now slowly drawn through the apparatus for about half an hour to remove any carbon dioxide which may be present. The caustic potash bulb is detached, thoroughly cleaned, and after standing in the balance-case for twenty to thirty minutes, is weighed. Whenever this bulb is detached, the hole in the stopper in the end of the long glass tube should be closed with a glass plug.

After replacing the weighed caustic potash bulb, introduce from 30 to 50 c.c. of dilute hydrochloric acid into the dropping-funnel. Open the stop-cock and allow the acid to flow into the flask at such a rate that not more than two bubbles of air per second pass through the caustic potash solution. After all of the acid has been introduced, close the stop-cock in the funnel and warm the flask gently, finally to boiling. A very small flame must be used at first to prevent the gases from passing too rapidly through the caustic potash solution. It must at all times pass slowly enough to permit the bubbles to be readily counted. When water begins to condense in the lower part of the long glass tube, the heating of the liquid should be stopped, the stop-cock quickly opened, and suction applied to the absorption-bulb. When the first violent flow of air into the flask has ceased, air is drawn through the apparatus at the rate of two bubbles per second for about three-quarters of an hour. For this purpose a Bunsen filter-pump may be used. The flow of air may be regulated by a screw pinch-cock. A better device consists of a large bottle filled with water which is led out through a siphon extending to the bottom of the bottle and passing through a doubly perforated stopper. Through the second perforation passes the tube connected to the carbon dioxide apparatus. The flow of water is controlled by a pinch-cock placed on a rubber tube at the end of the siphon.

The caustic potash bulb is disconnected, carefully cleaned, placed in the balance-case, and weighed. After replacing the caustic potash bulb, the solution of the dolomite is gradually heated to boiling again and air drawn through the apparatus in the same manner as before, after which the caustic-potash bulb is again disconnected and weighed to ascertain if all of the carbon dioxide has been swept out of the apparatus. If the operation has been properly conducted, not more than 2 or 3 mg. will be obtained on the second weighing. When sufficient experience has been gained the operation may be so conducted that only one weighing will be necessary.

CHAPTER XVI.

ANALYSIS OF SILICATES AND SEPARATION OF SODIUM AND POTASSIUM.

SEPARATION OF MAGNESIUM FROM THE ALKALIES.

IN the course of an analysis the other metals are first precipitated, leaving magnesium and the alkalies in solution. Magnesium may then be precipitated as phosphate and weighed. During the course of this determination alkalies are introduced into the solution so that it is not available for the determination of these metals. A different method of precipitation of the magnesium must therefore be adopted or a fresh portion of the unknown must be taken and the magnesium as well as the other heavy metals separated from the alkalies. The latter is by far the most satisfactory method of procedure, and is invariably adopted when sufficient material for analysis is at hand.

264. Separation of Magnesium by Means of Mercuric Oxide.—The magnesium may be removed without introducing alkalies by means of mercuric oxide. The solution of the chlorides from which other acids must be absent is treated with mercuric oxide which is free from alkalies. The operation should be conducted in a platinum dish. It is best to use freshly precipitated moist mercuric oxide. If much ammonium chloride is present, the solution should first be evaporated to dryness in the platinum dish and the residue gently ignited until ammonium salts are expelled. The residue is then dissolved in a little water and excess of the mercuric oxide added and the material well stirred. The solution is evaporated to dryness with frequent stirring. The residue is heated, at first gently and then more strongly, until mercuric chloride is no longer evolved. All of the mercuric oxide need not be volatilized. The residue is extracted repeatedly with small quantities of hot water and the solution rapidly fil-

tered. The washing must be discontinued as soon as the residue is free from chlorides.

By this operation the magnesium is converted into oxide according to the following equation: $\text{MgCl}_2 + \text{HgO} = \text{MgO} + \text{HgCl}_2$. The chlorides of the alkalies are not decomposed in this manner. As the magnesium oxide is slightly soluble, the solution of the alkalies will contain a little magnesium. Unless the amount of magnesium present is less than 1%, the treatment with mercuric oxide must be repeated. The insoluble mixture of magnesium and mercuric oxides may be ignited, the mercury volatilized, and the magnesium weighed as oxide. The magnesium may also be dissolved in hydrochloric acid after volatilization of the mercury and determined as phosphate. The mercuric oxide used must not leave a residue on volatilizing a portion by heating it to redness in a platinum dish or crucible. Alkalies are frequently present and remain as an alkaline residue after volatilization of the mercury. If mercuric oxide free from alkalies cannot be obtained the amount used must be weighed and a correction made for the amount of alkali present.

265. Separation of Magnesium by Means of Barium Hydroxide.—The magnesium may also be removed by treating the concentrated solution with a solution of barium hydroxide until it is strongly alkaline. After filtering off and washing the magnesium hydroxide the excess of barium must be removed from the solution of the alkalies by precipitation with ammonia and ammonium carbonate.

266. Separation of the Alkalies.—The solution of potassium and sodium chlorides is evaporated to dryness in a weighed platinum dish, finally on the water-bath. The residue must be heated to low redness to completely dry the chlorides before weighing. Two difficulties are met with in this process. The crystals of sodium and potassium chloride tend to enclose water so that on drying the material decrepitates with considerable violence, tending to throw the material out of the dish. The chlorides of sodium and potassium are volatile at a very low temperature. It is therefore necessary after evaporating on the water-bath to cover the platinum dish with a watch-crystal and transfer it to the hot-plate and dry as completely as possible before heating with the

Bunsen burner.



FIG. 26.

The burner must be held in the hand and the flame waved under the dish and removed as soon as any portion of the dish becomes red-hot. If the decrepitation is excessive, the watch-crystal on the dish may be inverted and the platinum dish placed in another of larger size. Any material which is thrown out

of the first dish is then deflected downwards into the second one.

The weighed chlorides are dissolved in water. A slight amount of insoluble matter which is usually present is filtered off on a small filter-paper and well washed. The paper is thrown into the platinum dish and ignited. The dish with the residue is weighed. This weight is subtracted from the weight of the dish and the dry chlorides. To the solution of the alkali chlorides enough platinic chloride is added to convert both the sodium and potassium chlorides into the chlorplatinic salts. The subsequent manipulation is the same as that given for potassium in Chapter VII. The sodium is found by difference.

DECOMPOSITION OF SILICATES.

The first step in the analysis of a silicate has for its object the breaking of the bond between the silica and the basic elements present, so that the latter may be brought into solution. As the silicates are among the most stable bodies found in nature, the accomplishment of this object is not always easy. When completely decomposed, or *opened up*, as the operation is sometimes termed, the analysis of the silicate involves only the ordinary problems of separation and determination.

267. Fusion with Alkali Carbonates.—By far the most largely used and perhaps the best method of accomplishing this object consists in fusing the very finely ground material with sodium carbonate or the so-called *fusion mixture*, which consists of sodium and potassium carbonates in the proportion of their molecular weights. This mixture fuses at a somewhat lower temperature than sodium carbonate alone. The result of this method of decomposition is that the silica is largely converted into sodium silicate, the silicic acid displacing the volatile carbonic acid in

the alkali carbonate. The bases remain as carbonates, or if a given base forms a carbonate unstable at the temperature of the fusion it will remain as oxide. The bases which have marked acid properties, such as aluminium, will combine more or less completely with the alkali.

268. Determination of Silica.—On treating the fused mass with water and acidifying with hydrochloric acid the alkali silicate is decomposed with liberation of silicic acid. The remaining alkali salts which are formed are also decomposed. On evaporating to dryness, to dehydrate the silicic acid, and again taking up with water and hydrochloric acid, all of the elements present go into solution with the exception of silica and part of the TITANIUM which is frequently present in silicates. It is seldom that the decomposition of the silicate and the solution of the bases in hydrochloric acid is so complete that the silica is absolutely pure. On the other hand, some of the silica goes into solution even after very prolonged drying.

To recover the dissolved silica, the filtrate is evaporated to dryness and the residue again taken up with water and hydrochloric acid. The most complete separation of silica is effected by heating the dry residue on the water-bath for one-half to one hour. If the residue is dried on the hot-plate or in the air-oven at a temperature above 100° , more of the silica tends to go into solution again. The residue after the first evaporation may be dried on the hot-plate. This is a more rapid method, and any silica which goes into solution will be recovered by the evaporation of the filtrate, the residue of which must be dried at 100° . A small amount of silica (1 to 2 mg.) goes into solution even after the second evaporation. This is precipitated with the iron and aluminium and may be recovered by dissolving these elements in acid-potassium sulphate, dissolving the melt in sulphuric acid, evaporating till fumes appear, diluting with water, and filtering.

269. Determination of Aluminium, Iron, and Titanium.—The aluminium and titanium oxides which are usually present with the silica may be recovered by treating the ignited and weighed precipitate with hydrofluoric and sulphuric acids and evaporating. In this manner the silica may be completely volatilized. Unless

sulphuric acid is present, some of the titanium will also be volatilized. After blasting, the residue is weighed and the correction applied to the weight of the silica. As the bulk of this residue is generally composed of titanium and aluminium oxides, it is advisable to combine it with the precipitate of aluminium, iron, and titanium hydroxides. After igniting and weighing, the combined precipitate is dissolved by fusing with acid-potassium sulphate. The iron is reduced by passing hydrogen sulphide through the water solution of the fusion. It is then determined volumetrically. The titanium is then oxidized by means of hydrogen peroxide and the amount determined by comparing the intensity of color with the color of a standard titanium solution. (See page 194.)

The other metals are separated and determined by methods which have already been described.

270. Decomposition of Silicates for the Determination of the Alkalies.—As alkalies have been introduced into the fusion mixture, these metals must be determined in a separate portion, which must be decomposed by a different method. One of the best of these methods is that of J. LAWRENCE SMITH. The silicate is decomposed by gently heating an intimate mixture of the silicate with 1 part of ammonium chloride and 8 parts of pure calcium carbonate. The alkalies as well as some of the calcium are converted into chlorides. Ammonia, the excess of the ammonium chloride, and carbon dioxide are volatilized. On treating with water, the chlorides of the alkalies dissolve, while the other bases together with most of the calcium remain undissolved. One advantage of the method is found in the fact that all of the magnesium remains in the insoluble residue, thus separating it from the alkalies. The calcium in the filtrate is precipitated with ammonia and ammonium carbonate and filtered off. The filtrate is evaporated to small bulk and a little more calcium precipitated with ammonium oxalate and filtered off. The alkalies in the filtrate, which now contains nothing but these metals as chlorides, are separated and determined by methods already given.

271. Decomposition of Silicates by Fusion with Boric Oxide.—Another method for decomposing silicates by which a solution is obtained in which all of the bases, including the alkalies, may be

determined, has been devised by JANNASCH and HEIDENREICH.* The flux is powdered boric oxide. It is prepared by recrystallizing two or three times the commercial article to free it from traces of alkali. The purified crystals are dried and fused in a large platinum crucible until free from water. By suddenly cooling the fused mass it cracks into pieces of a convenient size for powdering. The powdered material is kept in well-stoppered bottles, as it is hygroscopic.

Nearly all silicates are readily decomposed when mixed with 3 to 8 or more parts of this flux and heated, at first gently, and finally with the blast-lamp. The silicate must be very finely powdered, from one-half to one hour being taken for the grinding of 0.5- to 1-gram portions. A platinum crucible holding 45 to 60 c.c. should be used. After intimately mixing the silicate and the flux, gentle heat from a Bunsen burner is applied. Frothing and rising in the crucible is prevented as far as possible by stirring with a short platinum wire which does not reach above the edge of the crucible. When the material has been in quiet fusion for some time in the covered crucible, the flame of the blast-lamp is applied. From twenty to thirty minutes are generally required for the entire operation.

Some silicates like *andalusite*, *cyanite*, and *topaz* are not fully decomposed when heated with the flux by means of the blast-lamp. For these minerals more of the flux must be used, as high as 30 parts to 1 of the mineral being taken. After the preliminary heating with the Bunsen burner, a few additional grams of boric oxide are added and a flame which is fed by oxygen in place of air is applied. An ordinary blast-lamp is used with an opening $2\frac{1}{2}$ mm. wide. It is supplied with gas from at least 5 or 6 ordinary gas-cocks and the flame is made broad and free from luminosity. The heating is continued until the fusion is as transparent as glass.

272. Volatilization of the Boric Acid.—After fusion, the hot covered crucible is immersed in cold water until cold. The contents are then placed in a large porcelain or platinum dish and a saturated solution of hydrochloric acid in methyl alcohol is added

* Zeit. für anorg. Chem., Vol. XII, p. 208, 1896.

while the dish is covered with a watch-crystal. The crucible is rinsed with more of the methyl chloride and the solution in the dish is gently heated until, with occasional additions of the methyl chloride, solution is complete. This requires from ten to fifteen minutes. The solution is then boiled down to small bulk and evaporated to dryness on a water-bath in which the water is not quite boiling, so that the temperature in the dish is 80° to 85° . More methyl chloride is added and the heating at this temperature is continued until the boric acid is completely expelled. All of the metals will then be in solution as chlorides and may be separated and determined by methods already given.

This method of decomposing silicates has the advantage that a solution of the mineral is obtained which is small in bulk and free from the large amount of alkali salts which are introduced by the carbonate fusion. The separations of many of the metals are much cleaner and sharper in the absence of a large amount of the alkali salts. All of the metals, including the alkalies, may be determined in one portion. This is a decided advantage when only a small amount of the mineral is at hand. On the other hand, the purification of the boric acid, and more especially the uncertainty as to the complete decomposition of the mineral, are disadvantageous.*

EXERCISE 39.

Analysis of Feldspar, $(K_2O, Al_2O_3)(SiO_2)_x$.

Iron, Calcium, Magnesium, Sodium, and Titanium are also Usually Present.

273. **Decomposition of the Mineral.**—One gram of the finely powdered material is placed in a rather large platinum crucible and mixed with 5 grams of a mixture of 5 parts of sodium and 7 parts of potassium carbonate. The crucible is heated with the Bunsen burner until the mass is in quiet fusion and no more carbon dioxide is evolved. About one-half hour will be required. Seize the crucible with the tongs and cause the contents to solidify in a thin film around the sides of the crucible by giving it a rotary motion while the contents are cooling. Transfer the crucible to a beaker just large enough to allow the crucible to be placed on its side. Add enough water to cover the crucible and heat on the water-bath until the melt is disintegrated. Take out the crucible with a pair of tongs and rinse it well. The lid must also be well washed.

* For common errors in the determination of silica, see Jour. Am. Chem. Soc., 24 (1902), p. 262.

The material in the beaker should be examined for *undecomposed silicate* by rubbing the bottom with a glass rod. Any gritty substance is undecomposed feldspar. The main portion of the solution may be decanted and a little water added. When the material in the water is stirred up, undecomposed silicate settles quickly, while separated silica rises readily and settles slowly. When strong hydrochloric acid is added and the beaker is heated, undecomposed silicate does not dissolve. Filter it off on a small paper, wash, and add the filtrate to the main solution. Burn the paper and fuse the insoluble material with five times its weight of the mixture of sodium and potassium carbonate. The second fusion is treated exactly as the first. Failure to secure complete decomposition the first time is generally due to insufficient grinding of the silicate.

273. Silica.—Transfer the alkaline solution to a platinum or porcelain dish, cover with a watch-crystal and add excess of hydrochloric acid. The fused material may also be dissolved by the following method. The melt is poured into the crucible cover. As soon as redness has gone, and while still hot, slip the crucible and cover into a covered beaker containing enough dilute hydrochloric acid to neutralize the sodium carbonate. Solution is complete in a few minutes and most of the silicic acid remains in solution. Decant the solution if there is any undecomposed silicate which is filtered off and again fused.

The solution is evaporated to dryness on the water-bath and heated for at least one-half hour. Add 20 c.c. dilute hydrochloric acid and then heat on the water-bath until nothing more dissolves. About one-half hour is generally sufficient. Add 50 c.c. hot water, filter off the silica and wash a few times. Evaporate the filtrate to dryness and heat one-half hour on the water-bath. Add 20 c.c. dilute hydrochloric acid to the residue and heat on the water-bath until nothing more dissolves. Add 50 c.c. hot water and filter off the silica on the paper containing the main portion, and wash with hot water containing hydrochloric acid, and finally with pure water, until the precipitate is free from chlorides. Particular care should be taken to wash this silica very thoroughly. If it should turn black on ignition it indicates insufficient washing.

Dry the precipitate, transfer it to the weighed platinum crucible, fold the paper and place it on the precipitate. Cover the crucible and heat gently with the Bunsen burner until volatile matter is expelled, finally with the full flame of the Bunsen burner. Remove the cover, incline the crucible, and continue heating until the carbon is completely burned and the precipitate is pure white. Replace the cover and heat with the blast-lamp for fifteen to twenty minutes, cool, and weigh. Moisten the precipitate with a little water, add a few cubic centimeters of hydrofluoric acid and a drop or two of sulphuric acid. Evaporate the acid and ignite the residue with the blast-lamp. The weight of the residue must be subtracted from the weight of the silica. The aluminium iron precipitate is ignited in this platinum crucible together with the small residue from the silica precipitate.

275. Aluminium.—In the absence of manganese, the IRON, TITANIUM, and ALUMINIUM may be precipitated with ammonia and ammonium chloride. The precipitate must be redissolved and reprecipitated. If MANGANESE is present, the alkali fusion of the silicate will generally have a bluish-green color. Absence of this color is not proof of the absence of manganese. In the presence of manganese, the aluminium must be precipitated as basic acetate. The second precipitation, however, may be made by ammonia and ammonium chloride. These precipitations are carried out as directed on p. 157, Chapter XIII. On concentrating the two filtrates separately to a bulk of 75 or 100 c.c., a small precipitate of aluminium hydroxide sometimes separates out in one or both of the solutions. This is filtered off on a small filter-paper, the first filtrate being first passed through the paper, the second one being used to wash the first beaker and the filter-paper. The small precipitate is then redissolved in a little hydrochloric acid and reprecipitated, filtered off on the same paper, washed, and added to the main precipitate.

276. Iron.—After igniting and weighing the aluminium-iron precipitate, it is dissolved in acid-potassium sulphate, 3 or 4 grams of which are placed in the crucible, which is heated just high enough to melt the acid sulphate. Several hours' heating may be required to dissolve a large precipitate. When everything is dissolved, except possibly a little silica, the crucible is cooled and the contents dissolved in dilute sulphuric acid and the solution evaporated until fumes of sulphuric acid are evolved. Hot water is added and the silica is filtered off, ignited, and weighed. Its weight is to be subtracted from the weight of the alumina and ferric oxide. The solution is placed in an Erlenmeyer flask of about 250 c.c. capacity. The flask is fitted with a two-holed rubber stopper, a glass tube extending to the bottom of the flask being passed through one hole while a short glass tube is inserted in the other. The solution is heated nearly to boiling and hydrogen sulphide passed to reduce the iron. The excess of hydrogen sulphide is expelled by boiling the solution and passing a stream of carbon dioxide. When the hydrogen sulphide is entirely expelled, as indicated by lead-acetate paper, the solution is cooled, while the stream of carbon dioxide is passing and titrated with standard potassium-permanganate solution. The iron cannot be reduced by zinc, since the titanium would then be reduced also. After titrating the iron, the solution is suitable for the determination of titanium as described in the following paragraph.

277. Titanium.—The titanium is estimated by comparing the color of the unknown solution, after oxidation with hydrogen peroxide, with the color of a standard solution of titanium. The standard solution of titanium sulphate should contain 1 gram of TiO_2 per liter or the equivalent amount of titanium sulphate. 5% or more of sulphuric acid must be present in this solution. 10 c.c. are carefully measured out and mixed with 2 c.c. of 5% hydrogen peroxide free from fluorides and diluted to 100 c.c. in a measuring-flask. The solution to be tested is evaporated to about

75 c.c., transferred to a 100-c.c. flask, hydrogen peroxide added as long as the color is intensified, and the solution finally made up to 100 c.c. with dilute sulphuric acid. If the color of the solution is much more intense than that of the standard solution, it should be transferred to a larger flask and diluted with water and sulphuric acid. 50 c.c. of the standard solution is placed in a Nessler tube. The unknown solution is introduced from a burette into a second Nessler tube until the color seems equal to that of the standard. It is then diluted to 50 c.c. After shaking, the color is again compared with that of the standard. If the colors are not identical, a third Nessler tube is taken and a little more or less of the unknown solution is introduced as indicated by the first test. After diluting to 50 c.c., the colors are again compared. If the unknown solution is more dilute than the standard, the process is reversed. As 50 c.c. of the standard solution contains 5 mg. of TiO_2 , the volume of the unknown solution which gives the same depth of color will also contain 5 mg. of titanium oxide. The total amount may then be easily computed. The amount of aluminium oxide is found by subtracting the weight of iron found computed as Fe_2O_3 plus the weight of TiO_2 from the total weight of the precipitate.

278. The Manganese, Calcium, and Magnesium are separated and determined as given in Exercise 38, page 181.

DETERMINATION OF THE ALKALIES.

279. *Decomposition of the Mineral.*—For the estimation of the alkalies, 1 gram of the finely ground mineral is intimately mixed in a platinum crucible having a closely fitting cover with about 1 gram of resublimed ammonium chloride and 8 grams of calcium carbonate which is free from alkalies. The thorough mixing required is best effected by grinding together in a large agate or porcelain mortar the mineral and the ammonium chloride. The carbonate of lime is divided into four parts. Three of the portions are successively added and thoroughly mixed. The material is then transferred to the platinum crucible. The mortar is rinsed with the fourth portion of the carbonate of lime. The glazed paper, which should from the beginning be under the mortar, is then brushed off. The contents of the crucible are settled down by gently tapping it on the table. If a large enough crucible is not at hand, half the quantities may be used.

The crucible is covered and placed in an inclined position on a pipe-stem triangle. It is at first heated gently with the small flame of a Bunsen burner, placed so that the flame does not touch the crucible. As soon as the odor of ammonia is no longer perceptible, which should be after about ten minutes' heating, the crucible is heated to dull redness for not more than two-fifths of its height for forty or fifty minutes.

280. *Removal of Calcium.*—After cooling, the sintered cake, which is generally detached very readily from the crucible, is placed in a porcelain dish and 60 to 80 c.c. of hot water added. The crucible is washed out with

hot water and the cake is broken up with a blunt rod. The water is brought to a boil and after being allowed to settle, the solution is decanted through a filter-paper. The material in the dish is washed two or three times with hot water by decantation, finally brought on the filter-paper, and washed free from chlorides. The residue may be tested for unattacked mineral by dissolving in hydrochloric acid.

The calcium in the filtrate is precipitated by neutralizing with ammonia and adding ammonium carbonate and ammonia. The precipitation should be carried out in a platinum or porcelain dish and the solution should be heated nearly to boiling. After digesting some time, the precipitate is filtered off and well washed with hot water. The filtrate is evaporated to dryness in a platinum dish and the ammonium salts expelled. The residue is dissolved in a few cubic centimeters of water, a few drops of ammonium-oxalate solution added, and the small precipitate of calcium oxalate filtered off and washed.

281. Potassium and Sodium.—The filtrate, which now contains only sodium and potassium as chlorides and a little ammonium oxalate and chloride, is evaporated to dryness in a weighed platinum dish. The ammonium salts are expelled by gently heating the dish, covered with a watch-crystal, first on the hot-plate and then with the flame of the Bunsen burner. The dish must not be heated higher than to dull redness, and that only for a moment. The burner is held in the hand and waved under the dish. (See p. 187, § 266.) The residue is moistened with hydrochloric acid to convert any alkali carbonate into chloride. It is again evaporated to dryness, ignited and weighed.

When the alkali chlorides have been brought to constant weight they are dissolved in a few cubic centimeters of water and enough 10% platinum-chloride solution added to convert all of the alkali chlorides present into the double platinum salt. In this calculation, the amount of platinum solution necessary to convert the precipitate into the double chloride, if it were all sodium chloride, should be found and a little more than this amount added. The solution is evaporated to a syrupy consistency and about 50 c.c. of 80% alcohol added. The evaporation and subsequent manipulation must be carried out in an atmosphere which is free from ammonia fumes. The solid material is occasionally well stirred with a glass rod until no more solvent action can be observed. The solution is decanted through a Gooch crucible, which has been dried at 110° to 115°. More 80% alcohol is added, the precipitate digested and stirred, and the alcohol decanted. When the alcohol no longer becomes strongly colored, the precipitate is transferred to the crucible and washed with small portions of the 80% alcohol until it comes through colorless. Dry the crucible at 110° to 115° and weigh. The amount of potassium chloride is now computed and subtracted from the weight of the two chlorides to obtain the amount of sodium chloride present.

ELECTROLYTIC METHODS.

CHAPTER XVII.

THE IONIC THEORY; ELECTROLYTIC APPARATUS AND MANIPULATIONS.

THE separation of metals from their solutions and their electrolytic deposition in films which can be dried and weighed offers in the case of many metals rapid and accurate methods of determination, and while in many cases the time necessary for complete deposition of the metal is considerable, little or no attention from the operator is required. The methods in use have generally been empirically discovered without reference to the prevailing theories of the nature of electrolysis. The subject is made more intelligible when studied in the light of theories which serve to combine and harmonize all of the facts known.

282. The Ionic Theory of Electrolysis.—It is now generally believed that when the salt of a metal is dissolved in water, the molecules are separated by the water into at least two parts, which are electrically charged and are called *ions*. In the case of copper sulphate, the copper atom is separated as an ion from the remainder of the molecule, the sulphur and oxygen remaining in combination and constituting a second ion. The molecule of cupric chloride separates into three ions, one of which is the copper atom, while the other two are the chloride atoms. When an electrical current is passed through the solution, the *metallic* ions move *with* the current and tend to accumulate around the cathode, and are therefore called CATHIONS, while the ions composed of the *acid radicles* move in a direction *opposite* to that in which the current is moving and tend to accumulate around the anode, and are therefore called ANIONS. This separation of the constituent parts of a metallic salt is called electrolysis.

An ION may therefore be defined as a metallic atom, or an acid radicle, which is charged with positive or negative electricity and

exists in the solution of salts, bases, and acids, in water and a few other solvents.

283. Amount of the Electrical Charge on Ions.—According to Faraday's law the amount of a given metal which is deposited from a solution is proportional to the amount of current passed, provided no other decomposition is effected by the current. For example, a current of one ampere passing for one hour will deposit 4.026 grams of silver, any change in the amount of current passed producing a proportionate change in the amount of silver deposited. This would be the case if *each metallic atom or ion bore a fixed and definite amount of electricity*, since the current is carried through the solution only by means of the ions and when a given metallic ion gives up its load of electricity at the cathode it is deposited in metallic form.

As, still further, the amount of a given metal deposited by a current is inversely proportional to the valence of the metal, *the charge on each ion must be directly proportional to the valence*. A current of one ampere passing for one hour through a solution of cupric copper will deposit 1.184 grams of copper, while the same current passing for one hour through a solution of cuprous copper will deposit twice as much, or 2.368 grams of copper. An atom of copper present as cuprous chloride must therefore carry only half as much electricity as an atom of copper existing as cupric chloride. As the valence of the chlorine atom in these compounds is the same, and it is charged with negative electricity, the amount of this negative charge on each of the chlorine atoms must be the same since the solutions of both cuprous and cupric chloride are uncharged; that is, they contain the same amount of positive and negative electricity.

While the amount of a given metal deposited is proportional to the current used, the amounts of different metals deposited by the same current are directly proportional to the atomic weights and inversely proportional to the valence of the metals. The quantities $\frac{M}{n}$, $\frac{M'}{n'}$, $\frac{M''}{n''}$, etc., express the relative amounts of different metals deposited by the same current, where M , M' , M'' , etc., represent the atomic weights of the metals used and n , n' , n'' represent the valences of the metals as they existed in the solu-

tions used. Taking silver, cupric copper, and gold as illustrations, the relative amounts of the metals deposited will be in the ratio of 107.66, $\frac{63.18}{2}$, and $\frac{196.7}{3}$, or 107.66, 31.59, and 65.57. These numbers are in the same ratios as 4.026, 1.184, and 2.458, the amounts deposited by one ampere-hour of current.

In the language of the present electrolytic theory, an atom of *any metal* in the ionic condition carries a positive charge of electricity the amount of which is proportional to the valence of the metal and is the same for all metals of equal valence. All acid atoms or radicles carry a charge of negative electricity which is proportional to the valence and independent of the nature of the acid. Atoms of sodium, potassium, silver, and ammonium carry the same amount of positive electricity, while monovalent acid radicles such as chlorine, bromine, iodine, NO_3 , ClO_3 , etc., carry the same amount of negative electricity.

284. Potential of the Electrical Charge on Ions.—While the amount of the charge on all univalent atoms is the same, the potential is characteristic of the metal concerned. This may readily be shown by electrolyzing solutions of the various metals in which the same acid anion is present. The minimum difference in potential which must be impressed on the electrodes before a given metal will be deposited will be found to be characteristic of that metal.

The following minimum decomposition tensions were determined by LeBlanc for normal solutions:

	Volts.		Volts.		Volts.
ZnSO_4	2.35	NiCl_2	1.85	$\text{Cd}(\text{NO}_3)_2$. . .	1.98
NiSO_4	2.09	CdCl_2	1.88	$\text{Pb}(\text{NO}_3)_2$. .	1.52
CdSO_4	2.03	CoCl_2	1.78	AgNO_3	0.70
CoSO_4	1.92				

This peculiarity of the metals has been used to effect their separation. The metal which separates at the lowest potential is taken out first. On increasing the electromotive force of the current other metals may be deposited.

In a sulphuric-acid solution of cobalt and zinc, for example, the cobalt could be deposited by a current of an electromotive force less than 2.35 volts and greater than 1.92. After all of the

cobalt had been deposited the zinc could be deposited by increasing the electromotive force of the current to more than 2.35 volts.

285. Significance of Current Density.—Not only must the potential of the current used exceed a definite quantity before a given metal will be deposited, but the amount also of current used must be sufficiently large. The necessity for this is found in the fact that the deposited metal tends to redissolve in most of the solutions from which it is deposited. *The rate at which the metal is deposited must exceed that at which it redissolves.* As the rate at which the metal dissolves is proportional to the amount of surface exposed, the amount of current necessary to deposit the metal will depend on the area of the cathode surface. The amount of current per unit area, known as the *current density*, is therefore of importance in electrolytic determinations. The area generally used as the unit is 100 sq. cm., and statements of the amount of current necessary refer to the amount needed over such an area. The symbol ND_{100} is used for such a current density. The expression $ND_{100}=1.5$ amperes means that 1.5 amperes of current should be used for each 100 sq. cm., of cathode area.

As metals differ greatly in the ease with which they dissolve in a given acid, it is possible to so choose the strength of current to be used that with a given concentration of acid in a solution of two metals one will be deposited while the other will remain in solution. Copper and iron are generally separated in this manner.

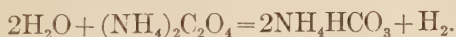
While the tendency of the metal to redissolve in the solution fixes a lower limit to the amount of current which may be used, the tendency of most metals to form deposits which are spongy and non-coherent when rapidly deposited prevents the use of an indefinitely large current. As the condition of the deposited metal is affected by the solution from which it is deposited, especially by the amount of acid present, and the temperature, the amount of current which may be used must be determined by experiment, the temperature, concentration, acidity, etc., of the solution being fixed.

286. Secondary Electrolytic Reactions of Acid Radicles.—The secondary reactions produced by the current frequently influence the electrolysis to a marked extent. Nitric acid is so rapidly

reduced to ammonia by a current of moderate strength, that the reaction may become strongly alkaline during the course of an ordinary electrolytic determination if a too dilute acid is used. Solutions of oxalic acid are entirely decomposed, hydrogen being given off at one electrode, while carbon dioxide is liberated at the other, the decomposition taking place according to the following equation:



If an oxalate of one of the alkali metals is present, the carbon dioxide is not evolved, but remains in combination with the alkali, the transformation from oxalate to carbonate being ultimately complete. The reaction with ammonium oxalate is as follows:



The chlorine set free during the electrolysis of hydrochloric acid or a chloride reacts with the water to form hypochlorous, chloric, and perchloric acids, which combine with the bases present to form salts. No secondary products are formed by the electrolysis of sulphuric acid and sulphates.

287. The Secondary Reactions Produced by the Metals are less numerous and complicated. The alkali- and alkaline-earth metals when deposited by the current react with the water present to form hydroxides, which combine with any acids present. Silver is almost always deposited from a solution of the double cyanide KAgCy_2 . In this compound the silver undoubtedly forms a part of the acid or negative radicle which is carried by the current to the anode. The silver, however, is found deposited on the cathode. This is explained on the assumption that the potassium which is liberated at the cathode displaces the silver in the cyanide radicle, one atom of potassium thus liberating one atom of silver. The deposits of some of the heavy metals, such as copper, are found contaminated with oxygen, while with others, as well as copper, hydrogen is occluded under certain conditions. Some of the metals, notably lead and manganese, are found deposited on the anode. These metals form negative ions which are deposited on the anode as most metals are on the cathode, or are oxidized

by the nascent oxygen liberated at the anode. The oxides formed in the case of manganese and lead, being insoluble in the nitric acid present, are deposited on the anode. The peroxides of manganese and lead formed in this manner may be dried and weighed as such. This property of manganese and lead offers an excellent method of separating these from many other metals. In this way the determination of two metals may be carried on simultaneously, one being deposited on the anode and the other on the cathode.

288. Reducing Current Strength by Means of Incandescent Lamps.—The electric current for quantitative work may be obtained in various ways. The ordinary commercial direct-current circuit of 110 volts is undoubtedly the most convenient, and where available the work is accomplished by such a current most satisfactorily and with the least labor. The current must, of course, be available the entire twenty-four hours of the day, as it is often most convenient to allow the electrolysis to continue overnight. The voltage mentioned is much greater than is ever required, and, as in reducing it part of the energy is wasted, a current of smaller voltage is more economical. The reduction of the current is very conveniently accomplished by means of incandescent lamps. If the current is passed through a 16-candle-power lamp about 0.4 ampere will be obtained. A 32-candle-power lamp will give a current of 0.8 ampere, while a 50-candle-power lamp will give a current of 1.2 amperes. The resistance of most solutions prepared for electrolysis is so small that when placed in series

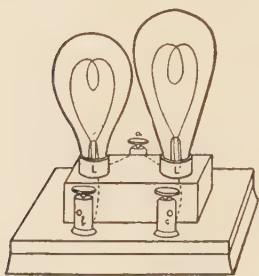


FIG. 27.

with the lamp the current is not materially reduced. A very convenient arrangement of the lamp-sockets is shown in Fig. 27. The lamp-sockets *L* and *L'* are connected to binding-posts *a*, *b*, and *c*, as shown in the figure, the various parts being screwed to a convenient sized board. By connecting at *a* and *b*, or at *a* and *c*, the current is passed through one lamp, while by connecting at *b* and *c* the current passes through both lamps in series, and by connecting *b* and *c* with a short piece of wire and passing the current from *a* to *b*, it passes

through the lamps in parallel. If 16-candle-power lamps are used, the single lamps give 0.4 ampere, the lamps in series give 0.2 ampere, while the two lamps in parallel give 0.8 ampere. The 32-candle-power lamps connected in the same manner give 0.8, 0.4, and 1.6 amperes respectively, while the 50-candle-power lamps give currents of 1.2, 0.6, and 2.4 amperes. Most electrolytic work can be done by these strengths of current.

289. Reduction of the Voltage of a Current.—If very small currents are desired they may most easily be obtained by making the electrolytic solution a shunt. If a 16-candle-power lamp is connected by means of a German-silver or other wire of several ohms resistance to the main circuit of 110 volts, any small number of volts desired may be sent through the solution by attaching the wires to two points on the resistance wire.

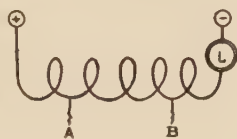


FIG. 28.

If the resistance between the two points *A* and *B* is about $2\frac{1}{2}$ ohms the difference of potential between these points will be about 1 volt. If about 5 ohms are enclosed between *A* and *B*, the difference in potential will be about 2 volts. In this manner any desired small voltage may be obtained. As OHM'S LAW holds for the solution, the current produced will be inversely proportional to the resistance. If, for instance, the resistance of the solution is 30 ohms and a difference of potential of 2 volts is desired at the electrodes the current obtained will be $\frac{1}{15}$ ampere according to Ohm's law, $C = \frac{E}{R}$,

C being the current, *E* the voltage, and *R* the resistance. If it is desired to increase the current while maintaining the difference of potential at 2 volts, the resistance of the solution must be decreased by warming it, or adding salts or acids or bringing the electrodes closer together or increasing their size.

290. Primary and Storage Cells.—A very convenient method of producing small currents is by the use of primary cells. Any desired voltage may be obtained by this means if a sufficient number of cells are provided. The cells used for this purpose should be those that give a current which is constant for a long period of time. The ordinary DANIELL gravity cell is cheap and gives a very steady current. The most satisfactory primary cell on the

market is the EDISON PRIMARY CELL, formerly known as the EDISON LALANDE CELL. The form known as type "S" is shown in Fig. 29. It has an electromotive force of 0.667 volt, and a capacity of 300 ampere-hours.



FIG. 29.

The positive plate is made of copper oxide and is placed between two zinc plates. The liquid is a solution of caustic soda which is protected from the carbon dioxide of the air by a layer of heavy paraffine-oil, which also prevents the solution from "creeping." The jar is made of porcelain, and is entirely unacted on by the alkaline liquid. No gases of any kind are evolved. The chemical reactions taking place may be represented as follows: $\text{Zn} + 2\text{NaOH} = \text{Na}_2\text{ZnO}_2 + \text{H}_2$. The hydrogen is oxidized by the copper oxide as follows: $\text{CuO} + \text{H}_2 = \text{Cu} + \text{H}_2\text{O}$. The current produced is very constant, although the potential rises slowly to about one volt as the copper oxide becomes reduced to metallic copper.

When a dynamo current is available which is not generated continuously STORAGE BATTERIES must be provided. If properly cared for, these cells give a very steady current, the small drop from about 2 volts when charged to 1.8 volts when discharged not affecting most electrolytic work, especially since adjustment may be made by resistance coils. Portable storage-cells may be purchased for use in laboratories where a dynamo current is not available. These cells may be carried to a power-station for charging.

When either primary or storage cells are used the strength of the current may be modified by varying the number of cells used, the voltage in every case being equal to the sum of the voltage given by the individual cells which are connected in series. The current may be still further regulated by inserting or removing resistance from the circuit. This is most easily done by means of a resistance-box connected in series with the solution to be electrolyzed.

A simple form of AMMETER and VOLT-METER are indispensable for much electrolytic work, especially in separations where a slight change of the potential may spoil a determination.

291. Use of Platinum Dishes as Cathodes.—Various forms of electrodes are in use upon which to deposit the metals determined. The most commonly used is an ordinary platinum evaporating-dish, such as is kept in most laboratories for other uses. Dishes of a capacity of about 150 c.c. and weighing 35 to 40 grams are most convenient. They should be free from scratches or dents produced by wear. Old dishes should be sent to the manufacturer to be reformed. The deposits of manganese and lead peroxides adhere more firmly to a platinum surface which has been roughened with a sand-blast. Such a rough surface may also be produced by depositing platinum electrolytically from a solution of potassium-platino-chloride by a rather large current. The deposit does not adhere very firmly unless, after washing, the dish is heated to redness for some time with the blast-lamp. Such a roughened dish is equally available for use with other metallic deposits than lead and manganese. As the dish cannot be employed for general laboratory purposes, it is advisable to roughen the surface of a platinum cone which is available only for electrolytic work.

The ANODES used with the platinum dishes are either disks of platinum to which a rod of the same metal has been securely fastened, or a stiff platinum wire the end of which has been made into a flat coil at right angles to the wire.

292. Electrolytic Stands.—The dish and anode are held by an electrolytic stand which is shown in Fig. 30, and consists of an iron base into which a stout glass rod has been fastened. A brass ring to which several platinum points have been soldered is attached to a clamp so that it may be fastened to the glass rod at any convenient height. A small binding-post is also fastened to the clamp for connection with the source of the electric current. A brass rod is fitted with a similar clamp for attachment to the glass rod. A binding-post for the second wire from the battery, or other source of electricity, is attached to the clamp. Another binding-post which can be moved along the brass rod holds the platinum anode.

For this rather expensive electrolytic stand various devices

made from ordinary laboratory apparatus may be substituted. An ordinary iron ring-stand is easily adapted to the purpose. A clean copper wire is wound around an iron ring of suitable size. The platinum dish is placed on this ring, the electric current being led to the dish by means of the copper wire. The stiff wire forming

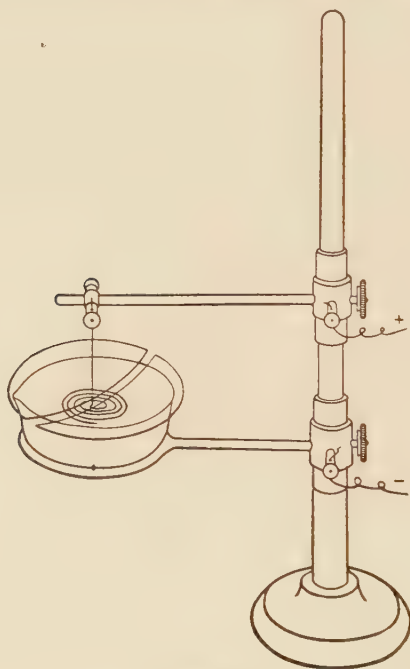


FIG. 30.

part of the anode is forced through a cork which is held in a clamp which in turn is fastened to the iron rod of the ring stand.

As considerable loss may result from the spattering of the solution due to the gases liberated by the electrolysis, it is advisable to cover the platinum dish with a watch-crystal through the centre of which a hole has been drilled. The watch-crystal is then split so that it may be placed on the dish with the anode passing between the halves where the hole was drilled. This watch-crystal must be rinsed off into the dish a short time before interrupting the electrolysis. A sheet of mica of suitable size is also convenient for this purpose.

293. Platinum Cylinders as Electrodes.—Platinum cylinders

made of thin foil and fastened to a stiff platinum wire are very largely used in laboratories where many electrolytic determinations must be conducted. The cylinders are made of two sizes, so that the one of smaller diameter may be placed within the other. The cylinders are of the same height. By carefully centering the cylinders, the space between them becomes of uniform width at all points, thus distributing the current so that the metal is deposited very uniformly. The larger cylinder is always connected so as to receive the metallic deposit. Instead of the inner cylinder, a

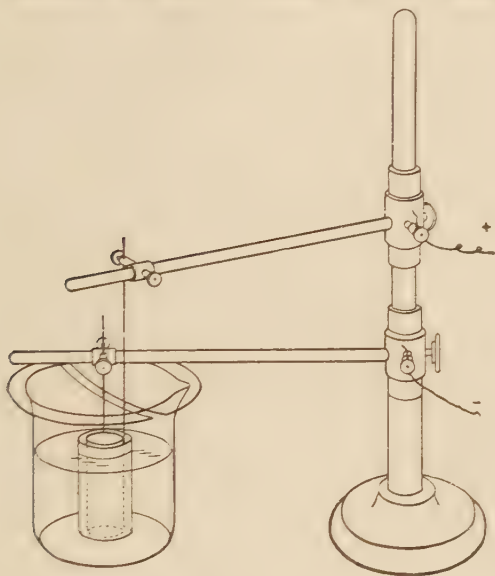


FIG. 31.

platinum wire either straight, or twisted into a coil, may be used. In place of the outer cylinder a truncated cone with the smaller end up has been used. Recently, cylinders made of *platinum gauze* have been found to offer many advantages over the forms already described. Not only is the time necessary for depositing the metal greatly shortened, but a much more firmly adhering deposit is obtained. The rapid deposition is undoubtedly due to the free circulation of the electrolyte permitted by the wire gauze. The firm adherence of the deposit is probably due to its cylindrical form, which does not give any point for the peeling process to start. *Rotation* of one of the electrodes, especially that on which the

metal is being deposited, has been found to improve greatly the quality of the deposit and shorten the time for complete deposition.

Supports for the cylindrical electrodes are made with an iron foot and glass standard, exactly like those used for the platinum dishes. Two brass rods similar to the one used for holding the anode for the dish are provided for holding the two cylinders. The use of cylinders has the advantage that the solution to be electrolyzed may be prepared in beakers, and in many cases insoluble matter need not be filtered off, nor the volume reduced by evaporation to that of the platinum dish.

294. Electrolysis of Warm Solutions.—The time required for many electrolytic determinations is greatly reduced by warming the solution. Temperatures from 60° to 80° are generally found suitable. This temperature need not generally be taken with a thermometer, since most chemists are able to estimate the temperature closely enough by touching the beaker with the hand. The small flame needed for this purpose may most easily be obtained by screwing off the tube of the Bunsen burner, and using the small white flame which is then produced by lighting the burner, and turning the gas nearly off. This white flame must not be allowed to come in contact with the bottom of the platinum dish. Starting the electrolysis with the solution warm will frequently insure a better deposit than can be obtained from a cold solution. The solution should be tested for the metal before interrupting the electrolysis unless the time required for similar determinations has been carefully noted. It is usually not advisable to allow the current to pass for a longer time than necessary to completely deposit the metal.

295. Washing and Drying Deposited Metals.—In many cases the deposited metal redissolves quite rapidly in the solution from which it has been deposited. In most cases the loss is very slight if the cylinders are removed from the solution while the current is passing and the acid is removed by instantly dipping them into distilled water or washing them in a stream of water. More accurate results are obtained, especially by the beginner, if the acid solution is replaced by water while the current is still passing. For this purpose, the acid solution is removed by a siphon, while a

stream of distilled water is poured in from the wash-bottle. If an incandescent lamp is used as resistance in circuit with the electrodes, the removal of the acid solution is indicated by the disappearance of light in the lamp. When the acid solution has been removed in this manner, the deposited metal is washed with distilled water and then with alcohol to remove the water. Ether is sometimes used for the same purpose, but it is much more liable to contain fatty substances in solution, which remain after evaporation of the ether. If ether is used, the metal will dry much more rapidly. The removal of the water is necessary, as moist metals oxidize rapidly and increase in weight. After washing with alcohol or ether, the metal is dried for a few minutes in the steam-bath, or in the air-bath kept at 100° , and after cooling, is weighed. The removal of the alcohol and the drying may be accomplished much more rapidly by burning the portion adhering to the surface. After cooling, the metal is weighed. A trifling amount of oxidation takes place when this method is used.

296. Rotation of the Anode or the Cathode offers several very decided advantages. The metal is generally deposited in a much smoother and more coherent film, so that a number of metals which cannot be deposited in coherent films with stationary electrodes can be successfully determined by rotating one of the electrodes. This character of the film also allows the use of a much larger current, so that the deposition is much more rapid. The agitation of the solution also increases the rate of deposition because the layer of liquid near the cathode is very soon deprived of its metal by the electric current when the solution is allowed to remain at rest, while when it is kept in constant motion, more metal is constantly being brought up to the electrode. For the same reason, heating the solution increases the rate of deposition because convection currents are set up in the liquid. Rotation of the cathode or anode produces a much more vigorous circulation and consequently hastens the deposition, so that 15 minutes is in many cases a sufficient time for the complete deposition of the metal.

297. Electrodes for Rotation.—Cylinders are not suitable electrodes for rotation. Platinum dishes, however, are admirably adapted for this purpose. The platinum spiral used as anode

can be very conveniently rotated, care being taken to accurately center the spiral and not to rotate it so fast that the solution is thrown out of the dish. Ordinary platinum crucibles may also be used for this purpose. A rubber or cork stopper is selected which fits tightly into the crucible. The shaft of the rotator is passed through a hole in the middle of the stopper, electrical contact being made between the shaft and the crucible. For this purpose a copper wire is wound around the shaft and passes through the hole in the stopper, projecting far enough to

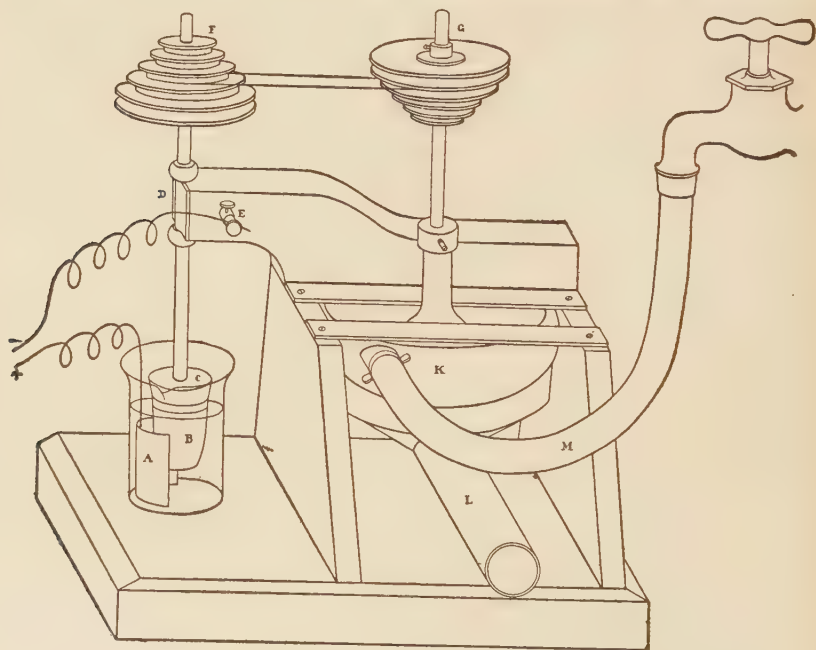


FIG. 32

touch the bottom of the crucible. Contact is made between the shaft and a binding post which is connected with the negative terminal. The positive terminal is connected with the anode, which may consist of platinum foil or wire. This arrangement is shown in Fig. 32. The metal is deposited on the outside of the crucible to within about a quarter of an inch of the top. When being weighed the crucible is inverted on the scale pan.

298. The Motors for rotation may be electric or water motors. A velocity of 300 to 600 revolutions per minute will be required.

A system of pulleys of different sizes is convenient for regulating the speed of rotation. In addition to this means of regulation, the current supplied to electric motors may be varied by changing

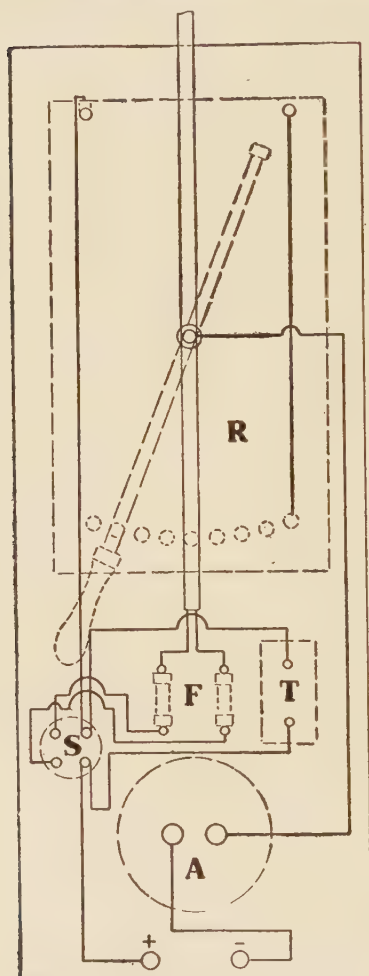


FIG. 34.

the resistance in the circuit, and with water motors the amount of water supplied is easily controlled. An apparatus designed for utilizing a water motor is shown in Fig. 32. The upright shaft of the motor rotates on a needle point, while the shaft holding the crucible rotates on the ball-bearings of a bicycle hub. An apparatus designed for using an electric motor is shown in Fig. 33. *R* is the resistance in circuit with the solution being electrolyzed and controls the amount of current used, as indicated by the ammeter *A*, which is in the same circuit. The fuses *F* protect the ammeter from being burned out. The motor *M* is attached by means of the flexible chord *C* at the socket *T*. The motor may be instantly stopped by pulling the chord out of the socket *T*. The motor requires no outside resistance. The switch *S* controls both the motor circuit and the electrolytic circuit, so that the electrolysis and the rotation may be started or interrupted

simultaneously. The wiring of this board is shown in Fig. 34, which is a diagrammatic representation of the reverse of the slate board upon which the apparatus is mounted. A volt meter has not been permanently connected with the other apparatus because in ordinary work it is not needed. The resistance *R* is in series with the electrolytic circuit, but not with the motor circuit.

CHAPTER XVIII.

ELECTROLYTIC DETERMINATION OF METALS.

DETERMINATION OF COPPER.

299. Deposition from a Nitric or Sulphuric Acid Solution.—The electrolytic determination of copper is, no doubt, the most accurate as well as the most rapid method of determining this metal. If the solution of copper is free from other metals, a great many of the methods which have been proposed may be used. If, as most generally occurs in practice, the copper must be determined in the presence of other metals but one or two methods are available. By these methods the copper is deposited from a solution containing **FREE NITRIC OR SULPHURIC ACID**. As the copper is apt to be deposited in a spongy form when only sulphuric acid is present, solutions containing only nitric acid, or nitric and sulphuric acids are generally used. Not more than 5% of concentrated nitric acid may be present, and if the same amount of concentrated sulphuric is present, $\frac{1}{4}$ % of concentrated nitric acid is sufficient. The sulphuric acid solution is used when the presence of the nitric acid or the ammonium salts formed by its decomposition would interfere with subsequent operations, such as the precipitation of zinc as sulphide.

The nitric acid may be entirely omitted if 1 gram of urea is added to the solution containing 7% to 10% of concentrated sulphuric acid. By using a current of about one ampere, the decomposition is then effected in less than two hours.*

300. Separation and Determination of Lead.—The sulphuric acid solution is used for copper when much lead is present. This metal is then separated as sulphate, in which form it may be filtered off and weighed. If only a small amount of lead is present, it may be deposited on the anode from a nitric acid solution, and

* Classen, *Quan. Chem. Analysis by Electrolysis*, page 160.

the peroxide washed, dried at 180° , and weighed. If the lead is to be separated and determined in this manner, sulphuric acid should not be introduced, as the lead peroxide will be contaminated with this acid.

301. Separation of Copper from Other Metals.—ZINC, COBALT, NICKEL, CADMIUM, MANGANESE, and moderate amounts of IRON may be present in the nitric acid solution without interfering with the accuracy of the determination of copper. Large amounts of iron are objectionable because the ferric salts tend to redissolve the precipitated copper. The difficulty is partially overcome by diluting the solution and increasing the current density. The copper may also be completely separated from iron by precipitation with hydrogen sulphide or sodium thiosulphate. The precipitate is filtered off, washed, and redissolved in nitric acid. From this solution it may be precipitated electrolytically and weighed.

SILVER, MERCURY, BISMUTH, ARSENIC, ANTIMONY, and TIN are deposited with the copper. Silver should be precipitated as chloride before electrolyzing the solution, an excess of hydrochloric acid being avoided. Mercury may be expelled from the ore by roasting. When alloys or ores of copper are dissolved in nitric acid the tin and almost all of the antimony remains undissolved while most of the arsenic goes into solution. The removal of these metals may be accomplished by passing hydrogen sulphide through the solution until no more precipitate is formed, and then dissolving the sulphides of arsenic, antimony, and tin in sodium sulphide solution. The copper sulphide may then be dissolved in nitric acid and the copper deposited and weighed.

Copper may also be readily and completely separated from BISMUTH, ARSENIC, ANTIMONY, and IRON by precipitation as *cuprous sulphocyanate*. The solution of the copper salt is made slightly acid with hydrochloric acid, and the copper reduced by saturating the solution with sulphur dioxide. A solution of ammonium thiocyanate is then added until precipitation is complete, and the mixture heated nearly to the boiling-point for a few minutes. The copper may also be precipitated by the addition of a solution of equal parts of acid ammonium sulphite and ammonium thiocyanate. The precipitate, which is colored when first formed, quickly becomes white, and settles very readily.

It is washed with warm water until free from the other metals present. The copper is dissolved in a little warm concentrated nitric acid, and then deposited as usual.

COPPER ORES containing ARSENIC, ANTIMONY, and TIN may be decomposed by fusion with six times the weight of a mixture of equal parts of sulphur and sodium carbonate or the same amount of dry sodium thiosulphate. The ore must be very finely powdered and the fusion conducted in a porcelain crucible. After heating with a small Bunsen-burner flame until sulphur is no longer evolved, the melt is allowed to cool, and then extracted with hot water, and the residue washed with water containing a little ammonium sulphide. By this treatment the arsenic, antimony, and tin are dissolved while the copper remains as sulphide, which is dissolved in nitric acid, and the copper in the solution determined.

302. Deposition of Copper from an Ammonium-oxalate Solution.—A very excellent method of determining copper is based on its separation from a solution containing excess of ammonium oxalate. Classen* has improved this method so that the determination may be carried out in two hours. As most of the metals are precipitated from an oxalate solution, this method cannot be used unless the copper is first separated from the other metals, or the amount present in a pure salt is to be determined.

EXERCISE 40.

Determination of Copper in Copper Sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

Clean, dry at 100° , and weigh a platinum dish or platinum cone or cylinder. Weigh out 1 gram of pure recrystallized copper sulphate. If the cone or cylinder is used, transfer the copper sulphate to a 250-c.c. beaker, otherwise place it in the weighed dish. Dissolve in a few cubic centimeters of water, add a solution of 4 grams of ammonium oxalate, and dilute the solution to about 120 c.c. Make a saturated solution of oxalic acid by dissolving 4 grams of the crystals in 50 c.c. of water, and filter if necessary. Place the dish on the ring of the electrolytic stand, and adjust the anode so that it is about $\frac{1}{4}$ inch below the surface of the liquid. If a beaker is used, it must be placed on a tripod or other support, so that the solution can be heated. The cylinder or cone should be adjusted so that it very nearly touches the bottom of the beaker. Fasten a burette by means of a

* Classen. Quant. Anal. by Electrolysis, page 154.

clamp and ring-stand, so that the solution of oxalic acid which is placed in the burette will drop on the split watch-crystal which covers the dish or beaker. A thermometer is also suspended with the bulb in the copper solution, which is heated with a small flame from a Bunsen burner to 80° . The current of electricity used should be so adjusted that about 1 ampere passes through the solution, and the tension at the electrodes is from 2.5 to 3.2 volts.

As soon as a film of copper is seen to cover the cathode, the stop-cock of the burette is so adjusted that the oxalic-acid solution falls at the rate

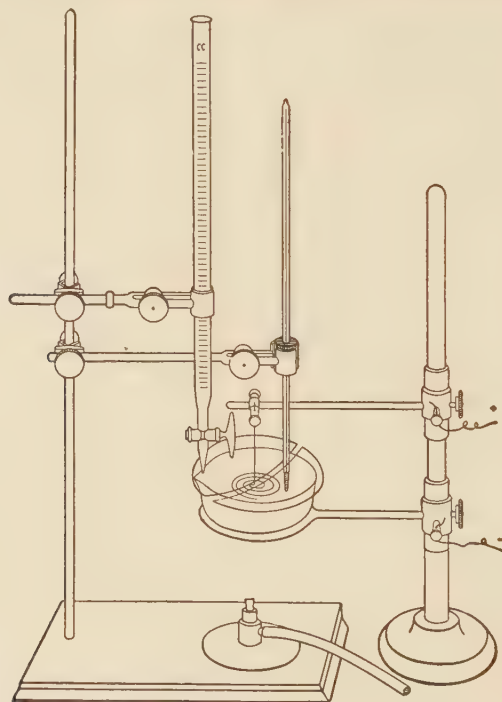


FIG. 35.

of 10 drops per minute. The copper comes down as a bright-red deposit. If it becomes dark-colored or spongy, the oxalic acid should be allowed to drop faster. The electrolysis will be completed within two hours. When the solution has become colorless, portions may be taken out and tested for copper by acidifying with hydrochloric acid and adding potassium ferrocyanide. When all of the copper has been deposited, siphon off the acid liquid while water from the inverted wash-bottle is allowed to flow over the copper deposit. The copper is then washed with alcohol, dried at 100° , and weighed. The theoretical percentage of copper in copper sulphate is 25.41.

EXERCISE 41.

Determination of Copper from a Nitric-acid Solution.

The copper in copper sulphate may also be precipitated from a nitric-acid solution. This method is well adapted to the determination of copper in the refined metal. About 0.3 gram of the metal is carefully weighed out, and dissolved in 3 c.c. concentrated nitric acid and a little water. The solution is diluted to about 100 c.c., and warmed to 50° or 60°, and the copper precipitated with a current of 0.5 to 1 ampere. No arrangement need be made to keep the solution warm, as in the preceding method. The deposition of the metal is more rapid, and a better deposit is obtained if the solution is warm at first. After four to five hours, all of the copper will be deposited. If a cylinder made of wire gauze is used, about half this time will be required. If the rotating cathode or anode is used, the amount of nitric acid may be reduced to 1 c.c., while the current may be increased to from 3 to 5 amperes. Most of the copper will be deposited in 10 minutes. The small amount still remaining in solution will be very rapidly deposited if the solution is nearly neutralized by the addition of ammonia. When all of the copper is deposited, as shown by the ferrocyanide test, the solution is displaced with distilled water while the current is passing, and the deposit washed with alcohol, dried, and weighed exactly as directed in the first method.

303. Deposition of Silver from a Potassium-cyanide Solution.—

Silver is determined electrolytically almost exclusively from a cyanide solution. The potassium cyanide used must be pure. Failure to obtain good results is frequently due to the use of impure cyanide. Another sample of cyanide should therefore be obtained and used. The current density should be less than 0.5 ampere. The electrolysis may be conducted at the ordinary temperature, though when heated to about 65°, the time required for a determination is very much reduced, so that two or three hours is generally sufficient. 3 grams of potassium cyanide are sufficient for 0.5 gram of silver. If other metals are present, the silver may be precipitated as chloride, which is then dissolved in the potassium cyanide. It is doubtful, however, if in this case the result would be more accurate or obtained more quickly than if the silver chloride were directly weighed.

304. Separation of Silver from Lead and Copper.—Silver may be separated from lead in consequence of the deposition of the lat-

ter on the anode as peroxide, when a solution containing 20% of concentrated nitric acid is electrolyzed. The separation of silver from copper is effected by electrolyzing a solution of the two metals in potassium cyanide by a current giving a tension between the electrodes of about 1.4 volts. When all of the silver has been deposited, the copper may be determined by adding nitric acid to the solution, and increasing the tension between the electrodes.

EXERCISE 42.

Determination of Silver in Silver Nitrate.

Weigh out 0.5 gram of pure dry silver nitrate, and dissolve in a few cubic centimeters of water. Dissolve about 2 grams of potassium cyanide in a small amount of water, and pour the silver solution into the cyanide solution. Either the platinum dish or the cylinders may be used as described under the determination of copper. Three Edison-Lalande cells connected in series or other source of electricity giving about 3 volts, should be used. The electrolysis requires about six hours, but the time necessary may be reduced by warming the solution to 65°, which is about the temperature the hand can bear for a moment without much discomfort. If the anode is rotated, a current of 2 to 3 amperes may be used, and the deposition will be complete in 10 to 15 minutes. The end of the operation is ascertained by testing a few drops of the solution by adding hydrochloric acid. The test should be made under the hood. Siphon off the solution while adding distilled water, rinse with alcohol, dry at 100°, and weigh. If the cyanide solution becomes quite dark on passing the current, the potassium cyanide is impure and the result is not apt to be correct. The determination should be repeated with another sample of the cyanide. The theoretical percentage of silver in silver nitrate is 63.51.

EXERCISE 43.

Analysis of a Silver Coin.

305. Solution of Coin.—When results within 0.1 or 0.2% of the theoretical have been obtained with silver nitrate, a coin is analyzed. Thoroughly clean a dime or other silver coin by rubbing with alcohol, ammonia, etc. Cut it into four or five pieces so that each piece weighs about 0.4 gram. Weigh one of the pieces carefully, and dissolve in a few cubic centimeters of a mixture of equal parts of water and concentrated nitric acid. This should be done in a small covered beaker. Warm the beaker on the water-bath, and when solution is complete remove the watch-crystal, rinsing it if necessary, and let the solution go to dryness.

306. Silver.—In the mean time weigh out roughly and dissolve in water two grams of potassium cyanide. Dissolve the copper and silver nitrates in a little water, and pour the solution into the cyanide solution. If difficulty is experienced in dissolving the salts of copper and silver which have dried on the sides of the beaker, a little potassium cyanide solution may be added after the water solution has been removed. The silver may be deposited on a platinum dish or on a cylinder. The solution should be warmed to about 65° , and electrolyzed with the current from two Edison-Lalande or similar cells connected in series. The difference of potential between the two platinum electrodes must be measured with a volt-meter and must not exceed 1.5 volts. If the two cells give a higher voltage than this, the potential must be reduced by introducing resistance. A resistance-box may be used, or the connection between the cells and one of the electrodes may be made by means of a few feet of German-silver wire. By drawing more or less of this wire through one of the binding-posts the resistance may be changed until the potential between the two electrodes is a little less than 1.5 volts.

The dish or beaker is covered with a split watch-crystal. As the evaporation at 65° is considerable, water must be added from time to time. In about five hours the electrolysis will be completed, as may be ascertained by adding water until an unplated portion of the platinum dish is covered. If no silver is deposited on this portion of the dish in half an hour, the deposition of the silver is complete. The solution is now siphoned off into a beaker and replaced with water, care being taken to lose none. The silver is rinsed with alcohol, dried at 100° , and weighed.

307. Copper.—The copper in the filtrate is deposited on a cone or cylinder after the addition of 5 c.c. concentrated nitric acid. The operation is repeated until analytical duplicates are obtained. The rotating anode may be used in this determination as well as in the determination of the silver.

DETERMINATION OF NICKEL AND COBALT.

Both nickel and cobalt are most easily determined electrolytically. The same methods serve for both metals. Where the two metals occur together, they are separated from the other metals present by the methods given in Chapter XIV. Both metals are then precipitated electrolytically, and, after weighing, the deposit is dissolved in nitric acid, one of the metals being precipitated and weighed by methods given in the chapter mentioned.

308. Ammonium-oxalate Method.—According to Classen* these metals may be readily deposited from a solution of the

* Classen, *Quan. Anal. by Electrolysis*, page 141.

double-ammonium oxalate. Nitrates and chlorides should be removed by evaporation with sulphuric acid. The excess of acid is neutralized with ammonia, and 4 to 5 grams of ammonium oxalate added, which is dissolved by warming the solution. Water is then added until the volume is from 100 to 120 c.c. If the temperature of the solution is kept at 60° to 70°, the electrolysis will be complete in three to four hours, a current of about 1 ampere and an electrode tension of 3 to 4 volts being used.

309. Ammonia Method.—By the method of Fresenius and Bergmann* chlorides and nitrates are removed by evaporation with sulphuric acid. The excess of acid is then neutralized with ammonia, and unless at least 6 c.c. of strong ammonia (sp. gr. 0.90) are used for this purpose, 6 grams of ammonium sulphate should be added. 15 c.c. of strong ammonia are then added, or if more than 0.5 gram of metal is present, 20 c.c. should be used. The solution is then diluted to 150–170 c.c., and electrolyzed with a current of 0.7 ampere. The separation is not hastened by warming the solution. The deposition is complete in about six hours.

EXERCISE 44.

Analysis of a Nickel Coin.

310. Solution of Coin.—Clean a nickel coin thoroughly by rubbing with sand or "Sapolio." Cut it into small pieces weighing about 0.4 gram. After weighing one of these pieces place it in a small beaker (about 150 c.c.), and add 10 c.c. dilute nitric acid. Warm the covered beaker on the water-bath until the metal is dissolved. Rinse off the watch-crystal, add 16 c.c. dilute sulphuric acid, and evaporate on the water-bath until no more nitrous fumes come off.

311. Copper.—If a cylinder is available, dilute the solution until the cylinder is nearly covered when immersed so as to very nearly touch the bottom of the beaker. Electrolyse with a current of about 0.8 ampere. If the solution is warmed to about 60°, the copper will be deposited in from four to six hours. If it is convenient to conduct the electrolysis overnight, a current of about 0.4 ampere should be used, and the electrolysis begun with a warm solution, which is then allowed to cool off. The end of the operation is ascertained by testing a small portion of the solution for copper by passing hydrogen sulphide. After boiling for a few minutes to expel

*Zeit. Anal. Chem., vol. 19, page 329.

the hydrogen sulphide, this portion may be returned to the beaker. The solution may also be tested for copper by adding water so that a clean portion of the cylinder is immersed. If no copper is deposited on this portion after half an hour, all of the metal has been deposited. When all of the copper has been deposited, the solution containing the nickel is siphoned off and replaced with water. The copper is washed with water and alcohol, dried at 100°, and weighed. The anode or cathode may be rotated, and the current largely increased, and the time required for the deposition reduced to less than half an hour.

312. Nickel.—The solution containing the nickel should be evaporated if the volume is more than 250 c.c. It is neutralized with ammonia, 15 c.c. of concentrated ammonia added, and the nickel deposited with a current of about 0.7 ampere. About five to six hours will be required. The solution is tested for nickel by adding to a small portion a little colorless ammonium sulphide, or passing hydrogen sulphide. If the nickel is deposited slowly, enough ammonia is not present and more must be added. The solution need not be siphoned off. The nickel is washed with water and alcohol, dried at 100°, and weighed. The determination is repeated with other portions of the coin until duplicates are obtained. The rotating anode or cathode may be used for the deposition of the nickel. The current may then be increased to 5 amperes, when the deposition will be complete in less than half an hour.

DETERMINATION OF TIN.

Tin may be deposited in a bright, crystalline, closely adherent form from solutions of the double-ammonium oxalate containing free oxalic acid. If the tin is obtained as the dioxide, it may be dissolved by fusing with 8 times its weight of caustic soda in a silver dish. The melt is dissolved in water, an excess of oxalic acid added and the solution heated until clear. Hydrogen sulphide is then passed to precipitate the silver which is filtered off, after which the solution is boiled to expel the hydrogen sulphide. Ammonium oxalate is then added, the solution warmed to about 65°, and electrolyzed with a current of 4 to 5 volts and from 0.5 to 1.5 amperes. For 0.3 gram of tin 9 to 10 grams oxalic acid and 4 grams of ammonium oxalate should be used. The tin is completely deposited in about 4½ hours. It is washed as usual with water and alcohol, and dried in the steam-bath. Excellent results are obtained with the rotating anode.

313. Dissolving Tin Deposits on Platinum.—Some difficulty is experienced in dissolving the tin which has been deposited on

the platinum. This metal tends to form an alloy with the platinum so that acids do not readily attack the tin. The difficulty may be overcome by first coating the dish or other electrode with silver or copper or a silver dish may be used for these determinations. The silver is deposited from a solution of silver nitrate in potassium cyanide, while the copper may be deposited from a solution of copper sulphate acidified with nitric acid. After a sufficiently thick coating has been obtained by either method the solution is decanted and the deposited metal washed and dried as usual for the determination of these metals. The best solvent for the tin is prepared by diluting concentrated nitric acid with an equal volume of water and then saturating with oxalic acid. After most of the tin has been dissolved by this solution the nitric acid is washed off with water and the cylinder or dish immersed in concentrated C. P. hydrochloric and allowed to remain for 5 to 6 hours.

It is advisable to keep cylinders used for the determination of tin immersed in concentrated C. P. hydrochloric acid when not in use. This acid will dissolve all the tin if allowed to act for a sufficient time.

DETERMINATION OF LEAD.

This element cannot be determined by deposition in the metallic form, because during the process of washing and drying it invariably oxidizes to a greater or less extent. Advantage is therefore taken of the fact that when a current of electricity is passed through a nitric acid solution of lead, it is converted into the peroxide which is deposited on the anode, and may be dried by heating to 180° – 200° . The platinum anode should be roughened according to the suggestion of A. Classen by means of a sand-blast, otherwise the deposit readily flakes off unless deposited very slowly and in small amount. *By this method the lead is separated from zinc, cobalt, nickel, iron, aluminium, copper, gold, mercury, antimony, and cadmium. Traces of silver and bismuth, if present, are deposited as peroxide with the lead.*

314. Conditions of Deposition of Lead.—The amount of nitric acid which must be present depends on the temperature of the solution and the amount of current used. If the electrolysis is carried out at the ordinary temperature, about 10% by volume of nitric

acid of sp. gr. 1.38 must be present, and a current of .05 amperes used, while if a current of 0.5 amperes is employed 20% by volume of the nitric acid must be present. The deposition of the lead is much more rapid at a temperature of 60° to 65°, but the amount of acid necessary at this temperature for a current of .05 amperes is 2% by volume; while for a current of 0.5 amperes 7%, and for 1.5 to 1.7 amperes 20% is necessary. The small current must be used when only smooth dishes or electrodes are available. If too little nitric acid is present, metallic lead will be deposited on the cathode. Hydrochloric acid should be absent from the solution, and only small amounts of sulphuric acid should be present, as it is partly precipitated with the lead peroxide. The rotating anode or cathode may be used to advantage.

The end of the operation is ascertained by adding water, so as to expose a fresh portion of the electrode. If lead is still present, a dark-brown deposit will be formed after a quarter to half an hour. The solution need not be siphoned off. The lead peroxide is washed with hot water and then with alcohol, and is dried for half an hour in an air-bath heated to 200°. The lead dioxide may be dissolved in hot dilute nitric acid to which a little oxalic acid has been added, or in dilute hydrochloric acid which has been saturated with sulphur dioxide. It may also be dissolved in dilute nitric acid after being converted into litharge by heating for a few minutes in the *oxidizing* flame of the blast-lamp or of a Bunsen burner.

315. Determination of Lead in Ores.—The electrolytic method is well suited to the determination of lead in ores. If possible the ore should be decomposed without the use of nitric acid, which converts any sulphur present into sulphuric acid. As has already been said, the presence of this acid in the solution introduces a slight error in the determination. A method of treating the ore, which is suitable for galena, is given by Medicus.* The finely powdered ore is dissolved in concentrated hydrochloric acid. Excess of caustic-potash solution (1:3), and if antimony is present, 1 to 2 grams of tartaric acid are added. The solution is warmed for a few minutes at 100°, and, after cooling and diluting with water, the lead is precipitated by passing carbon dioxide.

*Ber. d. Chem. Ges., 1892, p. 2490.

This will require about one and one-half hours. The lead carbonate is washed with hot water until free from chlorine, and is then dissolved in dilute nitric acid and the paper well washed. The lead in the solution is then deposited as the peroxide, as already directed.

DETERMINATION OF ZINC.

A large number of electrolytic methods have been proposed for zinc, very few of which have been found practicable. The difficulties attending the gravimetric determination of this metal have led to continued effort in this direction, until methods which appear to be successful have been devised which depend on the deposition of the zinc from a solution kept slightly acid with a weak organic acid.

316. Difficulty of Dissolving Zinc.—In the electrolytic determinations of zinc, the same inconvenience is met with as in the determination of tin, that the metal is dissolved with difficulty from the platinum electrode. The same remedy is adopted: namely, to coat the platinum with silver or copper, or to use silver dishes. The zinc may be dissolved, leaving the copper or silver, by warming with dilute sulphuric acid.

317. Ammonium-oxalate Method.—In the method proposed by Classen,* the zinc is deposited from a solution of the double oxalate of zinc and potassium or ammonium. To the neutral and concentrated solution of zinc about 4 grams of potassium or ammonium oxalate are added. Solution is effected by warming, and, if necessary, adding a little water. The solution is diluted to about 120 c.c., warmed to 50° or 60°, and electrolyzed with a current of 0.5 to 1 ampere with an electrode tension of 3.5 to 4.8 volts. After the current has passed for three to five minutes, a cold saturated solution of oxalic acid, or better, a 6% solution of tartaric acid is allowed to flow from a burette at the rate of about 10 drops per minute upon the watch-crystal which covers the dish or beaker. The end of the operation is ascertained by testing small portions of the solution with potassium ferrocyanide.

* Classen, *Quan. Analysis by Electrolysis*, p. 146.

The time required is about two hours. The deposit must be washed without interrupting the current.

318. Acetic-acid Methods.—A method proposed by Riche and modified by Smith* involves the use of a solution of zinc acidified with acetic acid. To the neutral solution of the zinc, from which ammonium salts should be absent, 1 gram^{it} of sodium acetate, $\frac{1}{2}$ to 1 gram of ammonium oxalate, and 0.3 c.c. of 99% acetic acid are added. The solution is heated to 65°, and a current of about 0.36 ampere and 4 volts passed, and the anode or cathode rotated. Add acetic acid occasionally, as zinc forms the best deposits from a nearly neutral solution. At the end of an hour the current is increased to about 0.7 ampere and 5 volts. Water is added so as to cover a clean silver surface with the solution. If no more zinc is deposited and the solution is acid, it is carefully neutralized by the addition of ammonia and the current passed for about fifty minutes longer. The condition of the solution which requires the addition of ammonia is usually indicated by the solution appearing as if full of bubbles. The complete precipitation of the zinc is ascertained by testing a portion of the solution with potassium ferrocyanide. The solution is then siphoned off and the deposited metal washed with water and alcohol, dried at 100°, and weighed.

319. Determination of Zinc in Ores.—In carrying out the determination of zinc in zinc ores, the finely powdered material is weighed out and dissolved in hydrochloric acid, or, if necessary, in nitric acid. In the latter case the nitric acid is removed by evaporation with a little sulphuric acid and the residue dissolved in water. If considerable quantities of copper, arsenic, antimony, etc., are present, hydrogen sulphide is passed through the solution and the precipitate washed with water containing hydrogen sulphide. If iron, cobalt, and nickel are absent, the zinc may be determined in the filtrate by the method of Classen. Iron does not interfere if the method of Smith is used, since small quantities are not carried down with the zinc, and large amounts would be precipitated as basic acetate on warming the solution.

* Jour. Am. Chem. Soc., Vol. XXIV, p. 1073,

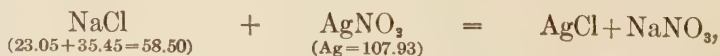
VOLUMETRIC METHODS.

CHAPTER XIX.

CALIBRATION OF APPARATUS.

320. Definition. — *Volumetric* are distinguished from *gravimetric* methods by the fact that in the former the amount of a given constituent is ascertained by MEASURING the VOLUME of a LIQUID, while in gravimetric methods, the element to be determined is brought to a condition where it may be placed on the balance-pan, and WEIGHED. Solutions of reagents which have been made to contain an accurately determined amount of a given chemical substance are called STANDARD SOLUTIONS. The volume of such a solution, which will just complete the reaction with a given constituent in a known amount of a substance to be analyzed, will give the amount of the constituent to be determined.

We may, for instance, weigh out 58.50 grams of pure sodium chloride and dissolve in a liter of water. The amount of silver contained in a given solution may be ascertained by adding the salt solution until all of the silver has been precipitated as silver chloride, and further addition of the salt solution gives no further precipitate. The volume of the salt solution having been carefully noted, the amount of silver present may be computed from the known amount of salt solution used. From the equation,



we know that 58.50 parts of sodium chloride can precipitate 107.93 parts of silver. As the salt solution contained 58.50 grams of sodium chloride per liter, if 100 c.c. were used to precipitate the silver, then 10.793 grams of silver were present in the unknown solution.

VOLUMETRIC APPARATUS.

321. Flasks.—The apparatus which has been devised for measuring the solutions consists in the first place of so-called standard flasks. These flasks are made of such a capacity that when filled to a mark made on the stem, they contain definite volumes of liquid, such as 1 liter or 1000 c.c., $\frac{1}{2}$ liter or 500 c.c., $\frac{1}{4}$ liter or 250 c.c., ect.

322. Pipettes are tubes constructed to deliver definite volumes having, generally, a bulb at the centre and a mark on the upper part of the stem to indicate the point to which the pipette must be filled to deliver the volume marked on the instrument. The liquid

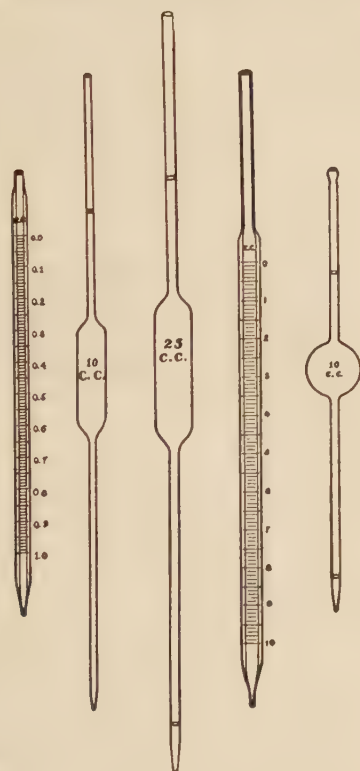


FIG. 36.

is sucked up into the pipette, the upper end closed with the finger, and after allowing the liquid to flow down to the mark, the contents of the pipette are allowed to flow into the desired vessel.

323. **Burettes** are glass tubes of uniform bore, having a stop-cock at the lower end, and marked so that any desired number of cubic centimeters may be measured out. The total capacity is usually

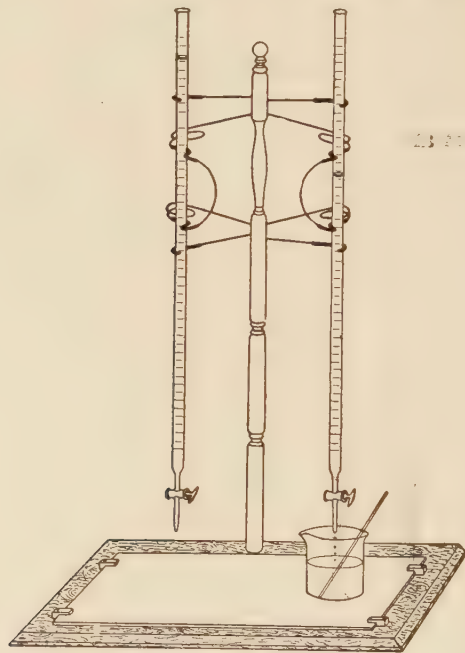


FIG. 37.

50 c.c., and the smallest divisions indicate either the fifth or the tenth of a cubic centimeter. It is customary to estimate the tenth of the smallest division so that volumes may be measured with burettes to the $\frac{1}{50}$ or the $\frac{1}{100}$ of a cubic centimeter.

324. **Reading Burettes.**—Unless special care is taken in making readings, errors of $\frac{1}{10}$ of a cubic centimeter may easily be made. Generally the lowest part of the meniscus is the point at which readings are made. As this point is in the centre of the tube, a different reading will be made according to the position of the eye, as will be seen from Fig. 38. One of the simplest devices for securing the correct position of the eye, corresponding to the point *b*, consists of a piece of paper or card with a perfectly straight edge folded double so as to completely surround the tube. The card is held so that the folded upper edges meet exactly, as shown

in Fig. 39. The eye is placed in such a position that the edge of the card on the front of the burette, the bottom of the meniscus, and the edge on the back of the burette are in the same line. The reading of the burette is then taken at the upper edge of the card. The eye may also be held in the same straight line with the upper edges of the meniscus. The lowest point of the meniscus

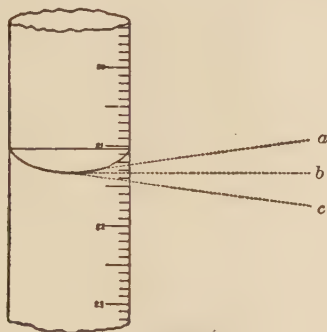


FIG. 38.

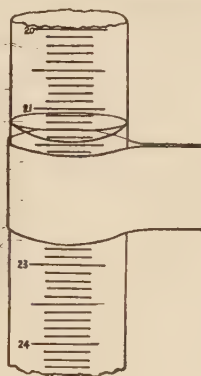


FIG. 39.

is then read. This method will give a reading which is slightly too high, but if the burette is always read in this manner, no error will result, as the volumes measured out are always found by taking the difference between two readings.

325. Floats.—Another method of securing accurate readings is by the use of floats, which are small glass tubes sealed at both ends and containing enough mercury to cause them to be very nearly immersed in dilute water solutions. A circle is etched on the float at right angles to its length, and the readings are made by the line which is produced by holding the eye in the plane of this circle. While this line gives very exact readings, serious error is often occasioned by the tendency of floats to go down irregularly by a series of jumps instead of following the level of the liquid. Before being used a float should be carefully tested by placing it in the burette filled with water. The water is allowed to flow out at a moderate rate, while the float is closely observed to see if it descends at a perfectly regular rate.

326. Errors in Reading Burettes.—When skill has been acquired in using one or the other of these devices and in estimating

the tenth of one of the smallest divisions on the burette, the accuracy acquired in practice is still never greater than $\frac{1}{1000}$ of a cubic centimeter; that is, the reading will be doubtful to the tenth of the smallest division of the burette. As an error of this magnitude is possible at both of the readings, in measuring a given volume of liquid the total error may be at least two-hundredths of a cubic centimeter. Careful experiments show that in careful work

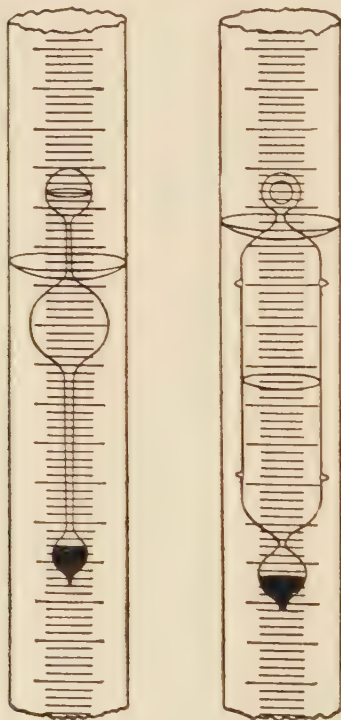


FIG. 40.

errors of three-hundredths of a cubic centimeter occur. The *percentage error* of a measurement is greater, therefore, the smaller the volume of liquid measured out, being 3% for 1 c.c., 0.3% for 10 c.c., and 0.1% for 30 c.c. As the possible errors in the other parts of volumetric analysis are not less than 0.1%, about 25 c.c. is the minimum volume of liquid which should be used in a volumetric analysis. Greater accuracy is seldom obtained by using a larger volume of liquid.

327. Method of Using Pipettes.—If a pipette is properly used, liquids may be measured with greater accuracy than is possible with a burette. This arises from the fact that the tube in which the initial and final readings are made is so much smaller than in the case of a burette. The errors in using a pipette arise from allowing the liquid to drain for varying intervals of time, and also from leaving a drop of liquid on the lower end of the tube. This drop should be taken off, when the liquid has been brought to the mark on the upper part of the stem, by drawing the point of the pipette along the glass surface of the vessel from which the liquid has been drawn. The liquid should be allowed to flow out of the pipette at its maximum speed, and the point should be touched against a glass surface when the pipette is empty. If it has a mark on the lower stem, the liquid must be allowed to flow to this mark; otherwise the pipette is completely emptied with the exception of the drop which always remains in the point. Some chemists blow this drop out of the pipette. This is unnecessary, but the amounts of liquid delivered will be identical if this practice is uniformly adhered to. More uniform results will be obtained if the hole at the point of the pipette is not over 2 mm. in diameter, so that the contents of the pipette may flow out in about ten seconds. If the opening is too large, it may be diminished by heating the point to redness in the flame of a Bunsen burner. The upper end of the stem as well as the finger used in closing it must be dry or the flow of liquid cannot be properly controlled.

328. Standard Temperature.—The volumes of the glass-measuring apparatus vary appreciably with changes in temperature, while the changes in the volumes of liquids is very marked indeed. It is necessary, therefore, in volumetric work to keep solutions and apparatus at some standard temperature. The most convenient temperature is that of the air in the laboratory. This changes within quite wide limits and varies in different countries. The German chemists have chosen 15° Centigrade as the average temperature of the laboratory. American laboratories are kept much warmer than this, so that 20° is a much better standard for this country. This will be used as the standard temperature for the work described in this book, the glassware being calibrated for this temperature.

329. Expansion of Glass, Water, etc.—The change in volume of a liter flask due to a change in temperature of 5° C. is 0.15 c.c. As this is .015% of the total volume, it is much less than other experimental errors and may, therefore, be entirely disregarded. The change in volume of water is much greater. A liter of water measured at 20° will contract 0.9 c.c. if cooled to 15° , while if heated to 25° it will expand 1.144 c.c. The error in this case for a change in temperature of 5° will therefore be about 0.1%. The change in volume of solutions is generally much greater, the more concentrated the solution the greater being the coefficient of expansion.

330. Errors of Graduation.—A very common source of error in volumetric analysis is the inaccuracy of the graduations of the measuring apparatus used. It is by no means uncommon to find errors amounting to 1% in apparatus bought of the dealers, while $\frac{1}{2}\%$ would, perhaps, fairly represent the error in using most untested apparatus. The errors are due to several causes, but chiefly to the fact that various standards of volume are in use.

331. Definition of Units of Volume.—Volumetric apparatus is usually constructed on the basis of the metric system, the units of volume being the LITER and the CUBIC CENTIMETER. In this system the unit of length was first selected and prepared. The unit of volume was obtained from the unit of length, a liter being defined as the cube whose sides are a decimeter in length. A cubic centimeter is the one-thousandth part of this volume. The unit of weight was obtained by preparing pure water and calling the weight of one liter weighed *in a vacuum* at 4° C. a kilogram.

332. Various Standard Liters in Use.—On account of the ease of preparing pure water, measuring its temperature correctly and weighing it with accuracy, the custom has arisen of using accurately weighed water as the standard of volume. This custom is still further justified by the fact that it is comparatively easy to obtain weights which are correct far beyond the accuracy attainable in measuring volumes. The errors found in commercial volumetric apparatus have arisen from a desire to avoid the trouble of making the weighings of the water under the standard conditions of temperature and absence of an atmosphere. In many instances the suggestion made by Mohr has been adopted.

He proposed to adopt as a liter the volume of 1 kilogram of water at 4° C., weighed in air. He adopted 17.5° C. as the standard temperature. This liter would differ from the true liter by 1.2 cubic centimeters. Other workers have used as a liter the volume of one kilogram of water weighed in the air at 15° C., while still others weigh at 17.5° C. or 20° C.

With these various standards in use it is not surprising, especially when taken in connection with the possible errors of workmanship, that the use of uncalibrated apparatus frequently produces very erroneous results. The possibility of error is considerably reduced if all of the volumetric apparatus in a laboratory has been made by the same manufacturer, since no error will result from the use of a standard other than the true liter if all of the apparatus is graduated according to the same standard, the cubic centimeter being exactly the one-thousandth part of the liter. Apparatus used for gas analysis must, however, be graduated according to the true liter. All confusion would be avoided if the true liter were generally adopted. The German chemists have taken the lead in this direction. The German Imperial Standards Commission has made it illegal to use any other than the true liter for official purposes. The directions given for calibration in this book will be based on the true liter.

CALIBRATION.

There are in use two general methods of calibrating volumetric apparatus. By the first method the weight and temperature of the water which just fills the apparatus to be calibrated is found and the volume calculated from the known density of water. By the second method standard bulbs whose capacity has been carefully determined are used. The water which just fills the bulb is allowed to flow into the flask to be calibrated. Where many pieces of apparatus must be calibrated this method is to be preferred.

333. Calibration of Flasks by Weighing Water.—Flasks which are to be calibrated are first cleaned and dried, then carefully counterpoised or weighed. Distilled water at 20° C. is poured in until the flask is filled to the mark. The additional weights necessary to again counterbalance the flask give the weight of the

water. The weight of the water *in vacuo* must now be calculated. The air displaced by a kilogram of water may be taken as a liter, which under ordinary temperatures and pressures weighs 1.2 grams. When in the air the water is lighter by this amount. The weights, however, are also lighter in the air than in a vacuum. The specific gravity of brass weights is 8.4. A kilogram of brass weights would displace $\frac{1.2}{8.4}$ of a liter of air which would weigh .14 gram. As the buoyant force on the water is 1.2 grams and on the weights .14 gram, the diminution in weight in the air is 1.06 grams (1.20 - .14). A kilogram of water, therefore, weighed in the air with brass weights would weigh 998.94 grams (1000 - 1.06), the weight in a vacuum being exactly 1000 grams. The general correction for air displacement is therefore +.106%. The weight of the water in a vacuum divided by the density at 20° gives the volume. In this manner the volume of the flask when filled to the mark is obtained. If a flask is to be calibrated to *deliver* a definite volume it should be rinsed with distilled water and allowed to drain for the same length of time employed in ordinary use. It is then weighed and the calibration carried out as already described.

If it is desired to ascertain the point on the stem to which the flask must be filled in order to contain one liter, it should be dried and counterbalanced on the scale-pan, and then weights equal to 997.2* grams placed on the opposite pan and distilled water at 20° C. poured into the flask until the weights are again counterbalanced. A mark may now be made with a file on the neck of the flask opposite the lowest point of the meniscus, and then a circular mark may be etched on by means of hydrofluoric acid. For this purpose a thin layer of paraffine or beeswax should be melted on the neck of the flask and a circle traced with a sharp steel point while the flask is rotated in a lathe or some similar device. The acid may be applied by means of a piece of filter-paper and should be allowed to remain from three to five minutes.

334. Calibration of Burettes by Weighing Water.—The burette is filled with distilled water at about 20° C. A small flask or

* 1000 c.c. water at 20° in a vacuum weigh 998.26 grams. From this weight the loss in weight of 1.06 grams due to air displacement must be subtracted.

weighing-tube capable of holding 50 c.c. is weighed. The water in the burette is now brought exactly to the zero-point and then about 5 c.c. is allowed to flow into the flask. The exact reading of the burette should be taken and the flask weighed. Another 5-c.c. portion of water is then allowed to flow into the flask and the burette again read and the flask weighed. This process is repeated until the last reading on the burette is exactly 50 c.c. and the flask contains the water delivered by the burette between zero and the 50-c.c. mark. The water need be weighed only to the hundredth of a gram, as volumes smaller than .01 c.c. cannot be measured on ordinary volumetric apparatus.

The volumes corresponding to the weights of water are now calculated by the method given for the calibration of a flask, .997 gram of water being equal to 1 c.c. The difference between the volume indicated on the burette and that calculated from the weight of the water is the correction to be applied at that point. The correction for intermediate points is found by plotting a curve, as shown in Fig. 44, in which the ordinates are the numbers 1 to 50 representing the readings on the burette, while the abscissas are the corrections found by the calibration. The assumption is made that the variations in volume are uniform between the points calibrated. Generally this does not lead to serious error. If the curve is very irregular, the burette should be calibrated for every 2 or 3 c.c.

CALIBRATION BY MEANS OF THE MORSE-BLALOCK BULBS.

335. Description of Bulbs.—If many pieces of apparatus are to be calibrated the Morse-Blalock calibrating bulbs should be used. These authors recommend the use of 6 bulbs of different sizes combined into 3 pieces of apparatus, as shown in Fig. 41. Three bulbs of capacities 2 c.c., 3 c.c., and 50 c.c., respectively, are all blown on one stem, various parts of which are graduated. Two bulbs of 50 c.c. and 200 c.c. capacity are connected on a single stem, which is also graduated, while the 500-c.c. bulb is on a separate graduated stem. Bulbs of other sizes could be made as desired. The intention of Morse and Blalock being to adapt the bulbs for use at a considerable range of temperature, they were

made of such a capacity that the volume of a bulb at 30° should not be greater than that marked on it, while at 0° the combined volume of the stem and bulb should not be less than that indicated on the bulb.

336. Calibration of the Bulbs.—The exact capacity of each bulb

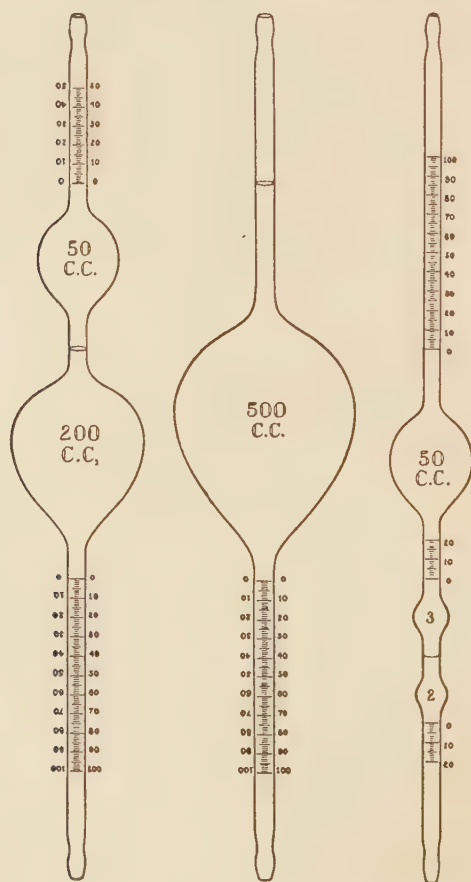


FIG. 41.

is ascertained by filling it with distilled water and weighing the amount delivered on emptying it. The temperature of the water is noted and the volume of the bulb for this temperature is calculated. The temperature of the water need not be that at which the bulb is to be used, since the volume of the bulb having

* been ascertained for a given temperature, by using the coefficient of expansion of the glass of which volumetric apparatus is made, .000026, the volume at any other temperature can be calculated. The volume of the graduated stem is ascertained in the same manner. In using a bulb for calibration it is filled with distilled water, which is allowed to flow into the dry and empty flask until the bulb and a sufficient number of divisions on the stem are emptied to give the required volume. An example will make this clearer.

Weight of Water from Bulb.		Calculated Volume.	
At 17.5°.	At 14.3°.	At 20°.	At 15°.
498.340 gr.....		499.51 c.c.	
	498.456 gr.	499.43 c.c.	
		Av. 499.47 c.c.	499.40 c.c.
Weight of Water from Stem.			
At 14.6°.	At 14.7°.		
3.177 gr.....		3.182 c.c.	
	3.180 gr.	3.185 c.c.	
		Av. 3.184 c.c.	

Volume of 1 division of stem = .032 c.c.

Bulb + 17 divisions of stem = 500.00 c.c. at 20° (499.47 + 17 × .032).

Bulb + 19 divisions of stem = 500.00 c.c. at 15° (499.40 + 19 × .032).

337. Temperature of Water Used in Calibration.—If it is desired to calibrate a flask to hold 500 c.c. at 20°, the water contained in the bulb and 17 divisions of the stem is allowed to flow into the flask and a mark made on the stem opposite the bottom of the meniscus. The temperature of the water need not be 20°. If the temperature of the water and consequently of the bulb is greater than 20°, the volume of the bulb and 17 divisions of the stem will be greater than 500 c.c., but on cooling to 20° it will be exactly 500 c.c. The temperature of the flask will be raised to that of the water, so that the volume of the flask will be greater than 500 c.c., but the flask also will contract on cooling, and as the bulbs are made of the same kind of glass as the flasks, *the contraction of the flask will be exactly equal to the contraction of the bulb.*

The same line of reasoning will show that the temperature of the water may be below the standard temperature without affecting the accuracy of the calibration.

338. Calibration of Flasks.—By means of the 50-c.c. and 200-c.c. bulbs, flasks of capacities which are multiples of 50 c.c. may be calibrated. For flasks whose capacities are multiples of 500 c.c., the large bulb is used.

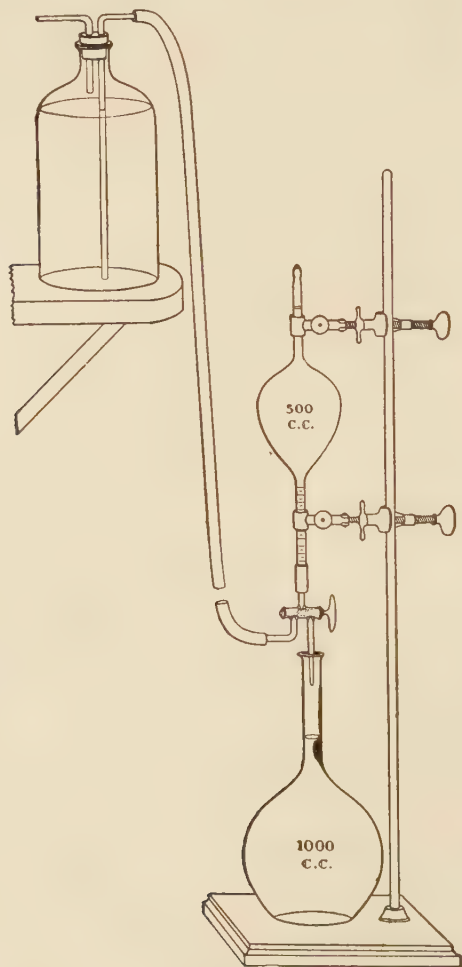


FIG. 42.

339. Calibration of Burettes.—The 50-c.c. bulb with 2-c.c. and 3-c.c. bulbs are used for calibrating burettes. For this work

as well as for calibrating flasks it is necessary to have a bottle holding several liters placed on a shelf which is above the top of the burette or bulb when fixed in clamps for use. A Friedrich-

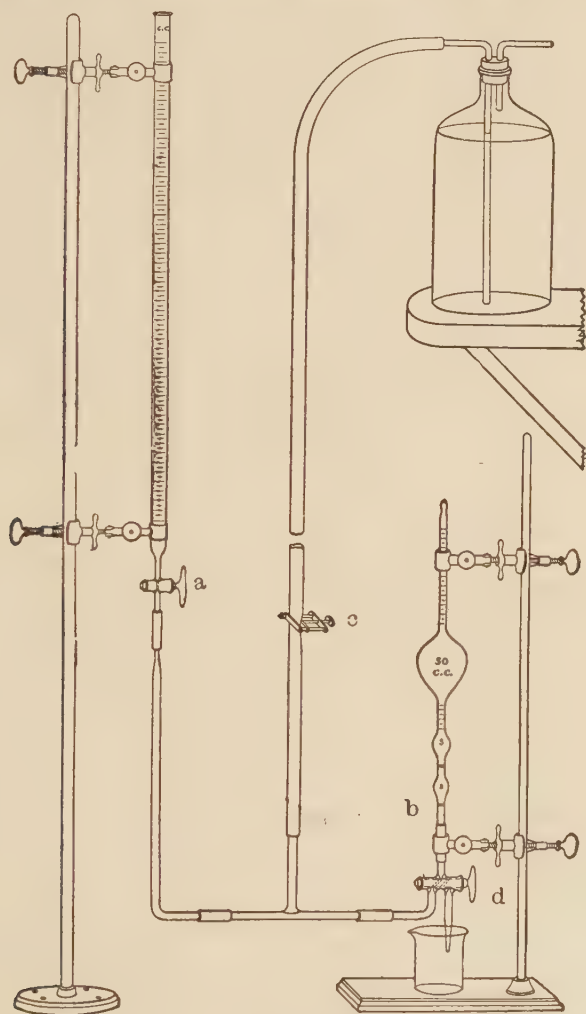


FIG. 43.

Greiner two-way stop-cock is attached to the bulb so that water may be withdrawn from the bulb by two openings in the stop-cock. One of these tubes is connected with one arm of a T-tube, the second arm being connected by a tube to the large bottle on

the shelf, and the third one is connected with the burette. The latter must be clamped in such a position that the point giving the last reading is above the highest point of the calibrating bulb. All joints must be absolutely water-tight, and the connecting tubes should be of glass as far as possible. A pinch-cock should be placed on the tube leading to the large bottle, which is filled with distilled water. By opening this pinch-cock water may be admitted either to the burette or to the bulb. All bubbles of air must be displaced from the connecting tubes.

340. Cleaning Mixture.—The burette and calibrating bulb must be cleaned so that a continuous film of water is left on emptying them. A most excellent cleaning mixture is made by adding a few grams of potassium dichromate to a half liter of concentrated commercial sulphuric acid. This mixture should be kept in a glass-stoppered bottle to which portions which have been used may be returned unless largely diluted with water. Apparatus filled with this mixture and allowed to stand for some time will be perfectly clean on pouring out the cleaning mixture and washing with water. The cleaning mixture is much more efficient if warmed. When it has become green because of reduced chromium, it must be discarded or more chromate added. Burettes and pipettes must always be kept clean or errors arise in their use because of the drops of liquid which adhere to the glass. If burettes are filled with distilled water when not in use, they keep cleaner than if left empty.

341. Total Capacity.—The bulb and burette are filled with water which is allowed to flow out at a moderate rate. The burette is again filled with water, and by cautiously turning the two-way stop-cock, water is allowed to flow from the burette into the bulb until the reading in the former is exactly zero. The stop-cock is now turned through 180° , and the 50 c.c. bulb emptied until the meniscus is opposite the mark on the stem. By again turning the stop-cock the water from the burette is allowed to flow into the bulb until the reading on the burette is exactly 50 c.c. The number of divisions of the stem of the bulb filled by the water is now noted. From this the total capacity of the burette can be calculated. Duplicates should agree within 1 or 2 divisions of the stem. The 50-c.c. bulb should be so constructed that its

volume is not greater than 49.75 c.c., while the capacity of the stem should be at least .75 c.c., so that the total capacity of the stem and bulb shall be about 50.50 c.c. If the capacity of the burette is greater than 50.50 c.c., the stem may be emptied, and water again allowed to flow in from the burette.

342. Irregularities of Bore.—The burette is once more filled with water which is brought to the zero-mark. It is then allowed to fill either the 2-c.c., 3-c.c., or both bulbs, depending upon the accuracy desired in the calibration. The reading of the burette is carefully taken, the small bulb emptied, and the operation repeated until the burette has been emptied. The capacity of the small bulbs should be a trifle less than that indicated, so that the last reading on the burette may always be less than 50 c.c. The method of calculating the results can best be given by the results of an actual calibration.

Total capacity = 50 c.c. bulb + 78 divisions of stem.

Total capacity = 50 c.c. bulb + 80 divisions of stem.

Volume of 50 c.c. bulb = 49.62 c.c.

Volume of stem (100 divisions) = .7807 c.c.

Total capacity of burette = 50.24 c.c. ($49.62 + .0078 \times 79$).

Readings.	True Capacity.	Corrections.
0.00	0.00	0.00
1.99	1.98	− 0.01
3.98	3.96	− 0.02
5.92	5.94	+ 0.02
7.90	7.92	+ 0.02
9.89	9.89	0.00
11.87	11.87	0.00
13.83	13.85	+ 0.02
15.81	15.83	+ 0.02
17.79	17.81	+ 0.02
19.77	19.79	+ 0.02
21.71	21.77	+ 0.06
23.68	23.75	+ 0.07
25.64	25.72	+ 0.08
27.60	27.70	+ 0.10
29.58	29.68	+ 0.10

Readings.	True Capacity.	Corrections.
31.55	31.66	+0.11
33.50	33.64	+0.14
35.48	35.62	+0.14
37.45	37.60	+0.15
39.40	39.58	+0.18
41.38	41.56	+0.18
43.32	43.53	+0.21
45.29	45.51	+0.22
47.28	47.49	+0.21
49.24	49.47	+0.23
50.00	50.24	+0.24

The last reading being 49.24 and the true capacity at 50.00 being 50.24, the true capacity at 49.24 is found by the proportion

$$50:50.24::49.24:x, \text{ where } x=49.47.$$

As the 2-c.c. bulb has been filled twenty-five times with water, the volume of which is 49.47 c.c., the capacity of the bulb must be $\frac{1}{25}$ of 49.47, or 1.979. As at each successive reading of the burette one bulb-full of water has been taken out, the true volumes at these points are found by multiplying 1.979 by the numbers from 1 to 25. These values are given in the second column. The differences between these values and the readings of the burette are the corrections to be applied at these points. The corrections are plotted on co-ordinate paper as abscissa, while the corresponding burette readings are the ordinates, as shown in Fig. 44.

EXERCISE 45.

Calibration of Morse and Blalock Bulbs.

Clean one of the bulbs by filling with bichromate solution and, after ten minutes, empty it and wash with water. Clamp it in position with the Greiner-Friedrich stop-cock, which is connected with the large bottle of distilled water, as shown in Fig. 42. Fill with water and allow it to flow out at a moderate rate. If the film of water left on the glass breaks, leaving drops, the cleaning with the bichromate solution must be repeated. When the bulb is clean, fill again with distilled water and bring the lower part of the meniscus exactly on a line with the upper mark on the bulb.

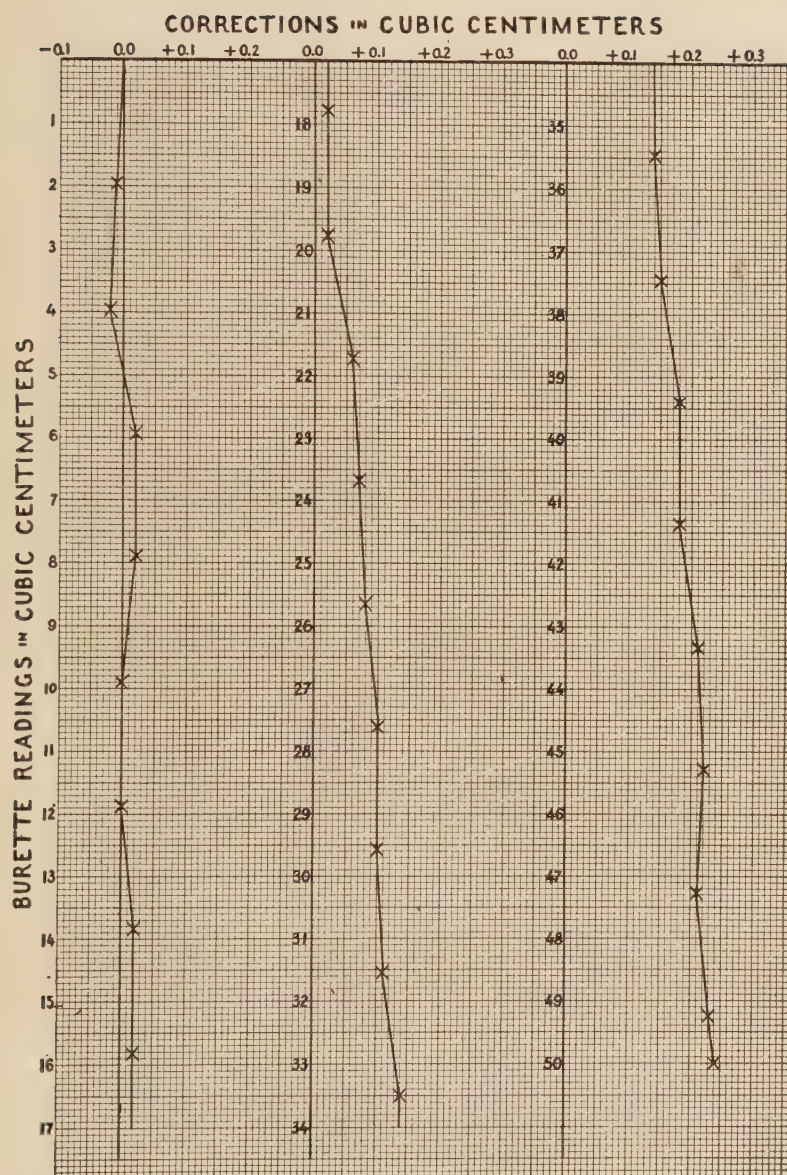


FIG. 44.

Let the water flow at a moderate rate into a weighed flask until the meniscus is at the lower mark on the bulb. Weigh the water to milligrams. Draw out another portion of the water into a flask and take its temperature. Repeat the determination until duplicates are obtained which are identical to at least 1 part in 1000. Calculate the volume using the specific gravity of water at the temperature noted and a correction of $+ .106\%$ for air displacement. Calculate the volume at 20° . In the same manner ascertain the volume of the graduated stem attached to the bulb. Calculate the number of divisions of the stem which must be used to make the volume equal to that marked on the bulb.

EXERCISE 46.

Calibration of Flasks.

Clean and dry the standard flasks you have. Clean all calibrating bulbs to be used according to the directions given in the preceding exercise. Clamp the $\frac{1}{2}$ -liter bulb in position as shown in Fig. 42. Fill the bulb to the upper mark and allow the water to flow into the liter flask until the bulb and the number of divisions on the stem giving 500 c.c. have been emptied. Repeat the operation and immediately make a mark on the neck of the flask opposite the bottom of the meniscus. Calibrate the other flasks in a similar manner. A thin layer of beeswax or paraffine should be melted on the neck and a circular line passing through the file-mark made with a sharp steel point. The flask should be held in a lathe for this purpose. The mark is etched on by dipping a piece of filter-paper into hydrofluoric acid and moistening the mark with the acid. After about three minutes the acid is washed off with water. After wiping the flask dry, the paraffine is melted by waving the neck of the flask in the Bunsen-burner flame. The neck of the flask may then be cleaned by wiping with dry filter-paper.

EXERCISE 47.

Calibration of Burettes.

After cleaning your burette, set it up with the 50-c.c. bulb as shown in Fig. 43, p. 239. Test the apparatus for leaks by filling with water and wiping all joints dry with filter-paper. No drops of water should be visible after fifteen minutes. All joints except *a* and *b* may be made tight by painting the glass tubing with shellac varnish before the rubber tubing is put on. The total capacity of the burette is first found by filling it with water by opening the stop-cock *c* and closing *d*. The water is carefully brought to the zero-mark by opening *a* (which should now remain open) and *d*.

The stop-cock *d* is now turned so that water can flow into the beaker until it is brought to the lower mark on the 50-c.c. bulb. *d* is again turned so that water is slowly admitted from the burette until it reads exactly 50 c.c. The number of divisions on the stem of the 50-c.c. bulb is now read. The determination is repeated until duplicates agreeing within 2 or 3 divisions of the stem are obtained. From the values already found for the 50-c.c. bulb, and for one division of the stem, the total capacity of the burette is calculated.

The burette is again filled with water and the reading brought to the zero-mark. If the total capacity is not more than 0.2 c.c. over 50 c.c., the burette may be calibrated every 5 c.c. For this purpose the meniscus of the water in the calibrating bulb is brought to the mark below the 2-c.c. bulb and water allowed to flow in from the burette until the 3-c.c. bulb is filled to the mark on the stem. The reading on the burette is now taken and the operation repeated until the burette is empty. Repeat the calibration until duplicates are obtained for each reading agreeing within less than .02 c.c. 10 portions of approximately 5 c.c., but *exactly equal*, will now have been withdrawn from the burette. The method of calculating the result is best given by the following example: A burette whose total capacity was found to be 50.15 c.c. gave as the last reading with the 5-c.c. portions 49.90 c.c. The volume at this point is found by the following proportion: $50.00 : 49.90 :: 50.15 : x$, from which x , or the volume of 10 of the 5-c.c. portions withdrawn, equals 50.05 c.c. Each 5-c.c. portion is therefore equal to 5.005 c.c. This number multiplied by the numbers from 1 to 10 gives the true volumes at the burette readings taken. The differences between the readings and the true volumes give the corrections to be applied at the points calibrated. To find the corrections at intermediate points, plot a curve with the corrections as the abscissas, and the readings on the burette as ordinates, as shown in Fig. 44. If the difference in the corrections between any two consecutive readings is more than .05 c.c., this portion of the burette should be recalibrated with the 2-c.c. or the 3-c.c. bulb.

PROBLEMS.

Problem 1. The weight of water at 20° C., which just fills a flask, is 249.2 grams. Calculate (a) the volume of the flask at 20°, (b) its volume at 15°, (c) its volume at 25°.

Problem 2. A burette was calibrated with a Morse and Blalock bulb, of which the 50-c.c. bulb had a capacity of 49.55, and the stem of 100 divisions had a capacity of 0.73 c.c. When obtaining the total capacity of the burette, the bulb was filled and 67 divisions of the stem. When calibrating the bore of the burette, 5-c.c. portions were withdrawn from the burette by means of the 2- and 3-c.c. bulbs. The following readings were obtained: 5.05, 10.09, 15.09, 20.19, 25.19, 30.19, 35.15, 40.19, 45.19, 50.10. Calculate the total capacity of the burette and the corrections at the readings given.

Problem 3. Another burette was calibrated with the same bulb. For the total capacity, the bulb full plus 70 divisions of the stem was obtained. When calibrating the bore of the burette, the following readings were taken: 5.00, 10.11, 15.09, 20.09, 25.08, 30.09, 35.05, 40.09, 45.10, 50.10. Calculate the total capacity of the burette and the corrections at the readings given.

The accuracy of the calibration of these burettes may be judged by a comparison of the volumes calculated for the 5-c.c. portions withdrawn from the burettes. These values should not differ by more than .03 c.c.

CHAPTER XX.

ACIDIMETRY.

343. A **Standard Solution** has already been defined as one which has been made so as to contain an accurately determined amount of a given chemical substance in a definite volume. It has been found that the acidity of a solution depends on the amount of replaceable or acid hydrogen present, irrespective of the amount of other substances present. A standard solution of an acid may therefore be defined as one which contains a known amount of acid or replaceable hydrogen in a definite volume. In practice it has been found very convenient to use standard solutions of acids which contain 1 gram* of replaceable hydrogen per liter. Such a standard solution is called a **NORMAL** solution. The strength of any standard solution may be given in terms of a normal solution. It may for instance be $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{10}$, etc., normal, or 3, $3\frac{1}{2}$, 1.362, etc., times normal.

344. **Normal Acids.**—The amount of a given acid to be dissolved in a liter to make a normal solution will vary directly as its molecular weight, and inversely as the number of acid or replaceable hydrogens in the molecule. **HYDROCHLORIC ACID** having a molecular weight of 36.458 (Cl=35.45, H=1.008), a liter of a normal solution of this acid must contain 36.458 grams of the acid. The molecular weight of **SULPHURIC ACID** is 98.076 (S=32.06, O₄=64.00, H₂=2.016). As the molecule, however, contains two replaceable hydrogen atoms, one-half of the molecular weight, or 49.038 grams, must be dissolved in a liter to make a normal solution. Normal solutions of all monobasic acids must therefore contain per liter the weight of acid equal to the molecular weight in grams, while

* Since the system of atomic weights having oxygen as 16.00 as the basis has come into use, 1.008 grams of hydrogen per liter has become the standard.

one-half the molecular weight in grams must be taken per liter for dibasic acids.

As the acid value of a solution depends wholly on the amount of replaceable hydrogen present, and as the designation of the strength of a standard acid in terms of normal gives the amount of hydrogen per liter, the weight of the acid radicle need not be known for calculating the results of a titration. If caustic soda is titrated with normal hydrochloric acid, one liter of the acid will neutralize exactly 40.058 grams of NaOH (Na = 23.05, O = 16.000, H = 1.008), according to the equation $\text{HCl} + \text{NaOH} = \text{NaCl} + \text{H}_2\text{O}$. If normal sulphuric acid were used the reaction would take place according to the equation $\text{H}_2\text{SO}_4 + 2\text{NaOH} = \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$. Two molecules of caustic soda or 80.116 grams per liter would be neutralized by one molecule of sulphuric acid or 98.076 grams per liter. But half of the latter amount having been taken for a liter of normal sulphuric acid, only one molecule of the caustic soda or 40.058 grams per liter of acid will be neutralized. It may be said then in general that a liter of a normal acid will neutralize 40.058 grams of caustic soda.

If sodium carbonate were being titrated only half of the molecular weight must be taken, as one molecule of this base is capable of replacing two atoms of acid hydrogen, the molecular weight in grams, 106.10, being able to replace 2 grams of acid hydrogen. One liter of normal acid is therefore equal to 53.05 grams of sodium carbonate. One-thousandth of this weight or the amount per cubic centimeter is more convenient for use in calculation, being .040058 gram of caustic soda and .05305 gram of sodium carbonate. If the strength of the acid must be expressed in fractions or decimal parts of normal, the value per cubic centimeter will be found by multiplying the value per cubic centimeter of a normal acid by the fractions or decimals. The value in caustic soda per cubic centimeter of $\frac{1}{10}$ normal acid will be $\frac{1}{10}$ of .040058 or .0040058.

When many titrations of a given substance must be made the calculation is simpler if the acid is so made that 1 c.c. is equal to an amount of base, which can be expressed by a simple number such as .050 gram of sodium carbonate. If such an acid is used for titrating any other substance, the calculation is not as simple as when the value of the acid is expressed in terms of normal.

345. Percentage Given by Number of Cubic Centimeters of Acid Used.—The calculation of the result for a single substance may be made very simple indeed if the acid is made of such a strength that the percentage is given by the number of cubic centimeters used in titrating a given weight of the substance. For instance, 1 gram of sodium carbonate requires for its neutralization .6872 gram of hydrochloric acid. This follows from the fact that 1 molecule of sodium carbonate (106.10) is neutralized by 2 molecules of hydrochloric acid (72.916). If a standard solution of hydrochloric acid is made of such a strength that it contains 6.872 grams of acid per liter, then 100 c.c. of this acid will just neutralize 1 gram of pure sodium carbonate. If mixtures of sodium carbonate and neutral salts are analyzed, the percentage of sodium carbonate will be given by the number of cubic centimeters of the acid necessary to neutralize 1 gram of the mixture. The strength of the acid in terms of normal may be found from the ratio of 6.872 to 36.458, which gives .1885 normal. As burettes holding 50 c.c. are commonly used, it will generally be found more convenient when mixtures containing more than 50% of sodium carbonate are to be analyzed to make the acid twice as strong. Then the percentage will be twice the number of cubic centimeters used. The same object will also be accomplished if acid of the same strength is used and $\frac{1}{2}$ gram of the material is weighed out for each determination.

The percentage may also be given by the number of cubic centimeters of a normal acid, provided a definite weight of the material is taken. In the case of sodium carbonate, 100 c.c. of a normal acid will be equal to 5.305 grams of the pure material, since, as has already been shown, one liter of the normal acid is equal to 53.05 grams of sodium carbonate. If 5.305 grams were weighed, the number of cubic centimeters of normal acid used would be equal to the percentage of sodium carbonate. It would be more convenient to weigh out 2.652 grams and multiply the number of cubic centimeters used by 2. If a fifth-normal acid were used, one-fifth or one-tenth of 5.305 grams would be taken.

INDICATORS.

346. Effect of Carbon Dioxide on Indicators.—The results obtained by titrating a given base with a given standard acid will differ according to the indicator used to give the end-point. This difference is due to the varying degree of sensitiveness of the indicators. For instance, a given amount of sodium carbonate will require about half as much standard hydrochloric acid for its neutralization if *phenolphthalein* is used as the indicator as when *methyl orange* is employed. This arises from the fact that when hydrochloric acid is added to a solution of sodium carbonate sodium chloride is produced and carbonic acid liberated. As carbonic acid is too weak an acid to change the color of methyl orange, the addition of the strong hydrochloric acid is continued until a slight excess is present, which gives the acid color to the indicator. Phenolphthalein, on the other hand, is sensitive to carbonic acid. Sodium carbonate reacts alkaline with phenolphthalein until, by the addition of a strong acid like hydrochloric, one-half of the sodium has been converted into sodium chloride, and the remainder is present as the bicarbonate. Another drop of hydrochloric acid liberates a little carbonic acid, which changes the color of the phenolphthalein. If the solution is concentrated or hot, carbon dioxide will escape, so that if the solution is boiled the titration of sodium carbonate will give the same result with either indicator.

As carbon dioxide is present in the air, in ordinary distilled water, and in most solutions of acids as well as alkalies, unless special precautions are taken to exclude it, the analyst must be thoroughly familiar with the behavior towards this acid of all indicators used. As has already been stated, methyl orange is almost entirely unaffected by it, while phenolphthalein is sensitive to one of the two hydrogen atoms of the acid. Carbonic acid may therefore be said to be monobasic to phenolphthalein in cold dilute solution. Its basicity is zero in boiling solution with phenolphthalein, as well as with methyl orange both hot and cold. Much valuable work on indicators has been carried out by R. T. Thomson,* who has divided them into three classes.

* C. N., v. 47, p. 123; 185, v. 49, pp. 32, 119. J. S. C. I., v. 6, p. 195.

The first class, of which methyl orange is the best example and the one most commonly used, comprises *lacmoid*, *dimethyl amido-benzene*, *cochineal*, and *congo red*. This class is *most sensitive to alkalis* and can be used with strong acids only, being unaffected by weak acids such as carbonic, silicic, etc. The second class, of which phenolphthalein is the type and the one most commonly used, includes also *turmeric*. These indicators are *extremely sensitive to acids*, and are therefore especially adapted to the titration of weak acids among which most organic acids must be placed. Strong bases must be used with these indicators, and carbon dioxide must be carefully excluded. The third class, of which litmus is the type, includes *rosolic acid* and *phenacetolin*. This class of indicators is about midway between the other two in sensitiveness, being fairly sensitive to both weak acids and weak bases.

347. Basicity of Acids with Various Indicators.—The table on page 252 prepared by Thomson gives the number of molecules of a univalent base, such as caustic soda or potash, neutralized by a molecule of each acid in the presence of the indicator at the head of the column. A blank indicates the absence of a sharp end-point. The same results are obtained with calcium or barium hydrate where insoluble compounds are not formed.

348. Litmus, although one of the earliest indicators used, has by no means been superseded by the many indicators recently introduced, especially by the workers in organic chemistry. It is considerably more sensitive than methyl orange, not only being more sensitive to weak acids, but giving an end-point more readily distinguished by most workers. Carbon dioxide interferes seriously, so that to obtain the best results this acid must be quite completely excluded. This may be readily done by boiling the solution. This operation does not destroy the indicator, but as it is considerably more sensitive cold than hot, the solution should be cooled before the titration is completed. For this reason methyl orange is more commonly used when considerable carbon dioxide is present.

As obtained in commerce litmus consists of small cubes composed of powdered chalk saturated with the coloring-matter, which is a vegetable extract. The coloring-matter is not a single

Acids.		Methyl Orange.	Phenolphthalein.		Litmus.	
Name.	Formula.	Cold.	Cold.	Boiling.	Cold.	Boiling.
Sulphuric.	H_2SO_4	2	2	2	2	2
Hydrochloric.	HCl	1	1	1	1	1
Nitric.	HNO_3	1*	1	1	1	1
Thiosulphuric.	$\text{H}_2\text{S}_2\text{O}_3$	2	2	2	2	2
Carbonic.	H_2CO_3	0	1 dilute	0	..	0
Sulphurous.	H_2SO_3	1	2	..	..	..
Hydrosulphuric. .	H_2S	0	1 dilute	0	..	0
Phosphoric.	H_3PO_4	1	2	..	..	..
Arsenic.	H_3AsO_4	1	2	..	..	..
Arsenious.	H_3AsO_3	0	..	..	0	0
Nitrous.	HNO_2	indicator destroyed	1	..	1	..
Silicic.	H_4SiO_4	0	..	..	0	0
Boric.	H_3BO_3	0	†	..	..	..
Chromic.	H_2CrO_4	1	2	2	..	..
Oxalic.	$\text{H}_2\text{C}_2\text{O}_4$	..	2	2	2	2
Acetic.	$\text{HC}_2\text{H}_3\text{O}_2$	..	1	..	1 nearly	..
Butyric.	$\text{HC}_4\text{H}_7\text{O}_2$	..	1	..	1 nearly	..
Succinic.	$\text{H}_2\text{C}_4\text{H}_4\text{O}_4$	..	2	..	2 nearly	..
Lactic.	$\text{HC}_3\text{H}_5\text{O}_3$	..	1	..	1	..
Tartaric.	$\text{H}_2\text{C}_4\text{H}_4\text{O}_6$	..	2	..	2	..
Citric.	$\text{H}_3\text{C}_6\text{H}_5\text{O}_7$	..	3	..	..	..

* Concentrated nitric acid sometimes contains oxides of nitrogen, producing on dilution nitrous acid which destroys methyl orange.

† 1 in a solution containing 30% of glycerine, or a few grams of mannitol. substance. Various methods have been proposed for obtaining the pure coloring-matter for use as a sensitive indicator. One of the simplest and best methods consists in extracting the cubes two or three times with hot 85% alcohol. By this treatment a violet coloring-matter is removed. The residue is then extracted several times with water, the first portion being rejected, as it contains the bulk of the alkali carbonates. The remainder of the water-extract is acidified with dilute sulphuric acid and boiled for some time to completely expel carbonic acid. The excess of sulphuric acid is then neutralized with barium hydrate. The neutral color is violet, which a drop of alkali turns to a decided blue, and a drop of acid to a decided red. The solution should be

preserved from mould by the addition of a few drops of chloroform. If kept in a closely stoppered bottle, the color disappears, but is restored on exposure to the air. The solution is best preserved in a wide-mouthed bottle partially filled, and protected from dust by a cover of filter-paper, or a loose cork stopper, through which passes a glass tube with which to withdraw the solution as needed.

349. Cochineal solution is very similar to litmus solution. When acidified the color is red, which is turned to violet by alkalis. It is not as sensitive to carbonic and weak organic acids as litmus. This gives it an advantage over the latter, as carbon dioxide need not be so rigidly excluded. It cannot be used, however, in the presence of even traces of compounds of iron or aluminium or acetates. It is used largely in the titration of ammonia in the Kjeldahl method for determining nitrogen. The solution is made by digesting 1 part of the crushed cochineal with 10 parts of 25% alcohol.

350. Methyl Orange is the sodium or ammonium salt of para-dimethyl-aniline-azo-benzene-sulphonic acid. It is a synthetic product, and can generally be purchased in a sufficiently pure condition for use. It is dissolved in water, 1 gram per liter giving a solution of which 1 drop is sufficient for most titrations. A large amount of this indicator decreases the sharpness of the end-point. An amount just sufficient to give a faint yellow color to the alkaline solution should be used. The solution should be kept in a bottle provided with a stopper, through which a drawn-out glass tube passes so that the indicator may be introduced by drops.

Methyl orange is very largely used because it is comparatively *unaffected* by carbonic acid as well as by *sulphuretted hydrogen*, *hydrocyanic*, *silicic*, *boric*, *arsenious*, *oleic*, *stearic*, *palmitic*, and *carbolic* acids, etc. The base in the salts of these acids may be titrated without removal of the acid. It has found a very extended use in the standardization of acids by means of pure sodium carbonate. In the presence of carbonic acid the change from the yellow alkaline to the red acid color is somewhat gradual. It is difficult to remember the exact shade corresponding to the neutral point, especially as a slight reddish tint is imparted by

the carbon dioxide. It is therefore advisable to prepare a solution for comparison which is given this tint by using distilled water saturated with carbon dioxide which has been freed from mineral acid by passing through a solution of sodium bicarbonate. The beaker containing this solution should be of the same size and contain the same volume of water as the beaker in which the titration is made. The same amount of indicator is also added. At the end-point of the titration a color a little deeper than that of the carbon dioxide solution must be obtained. The indicator is most sensitive in a cold solution. The presence of alcohol greatly decreases its sensitiveness. It cannot be used in solutions containing nitrous acid, as this acid destroys the indicator. If only small amounts are present, the titration may be completed before the indicator is destroyed. If large amounts are present, excess of standard alkali must be added, and the solution titrated back with standard acid.

351. Phenolphthalein is a synthetic organic product which may readily be purchased in a pure condition. It is dissolved in 90 to 95% alcohol, 1 or 2 grams per liter. It is advisable to first distil the alcohol after adding a little caustic soda or potash, as the commercial product is seldom free from organic acids. One or two drops of this solution are used. In neutral or acid solutions it is colorless, but the faintest excess of alkali gives a sudden change to purple-red. Carbon dioxide must be entirely absent, as in its presence the indicator reacts acid until it is converted into the bicarbonate by the alkali. Small amounts of carbonates in presence of alkali hydrates may be titrated accurately by means of phenolphthalein. Acid is added until the pink color has disappeared. All of the alkali hydrate will then be neutralized, and the alkali carbonate converted into bicarbonate. On adding methyl orange and standard acid until the red acid color of this indicator is developed the bicarbonate will be decomposed. From the amount of acid added for this purpose the amount of carbonate originally present may be calculated. The amount of carbonate must be small, as even the bicarbonate gives a slight color to the phenolphthalein.* Ammonia must

* Küster, Zeit. f. anorg. Ch., 13, 127.

also be absent, as in its presence the end-point is not sharp. Phenolphthalein is especially valuable for the titration of *weak acids*, especially the *organic acids*. Many of these acids being insoluble in water are dissolved in alcohol and then titrated. This does not seem to be quite as accurate as titration in water solution. A strong base must always be used with phenolphthalein. As water solutions of caustic soda and potash always contain carbon dioxide, an alcoholic solution of the latter is sometimes used, and more frequently a solution of barium hydrate.

352. Best Acid for General Use.—As has already been said, the acidity of a solution depends only on the amount of replaceable hydrogen present in a given volume, irrespective of the nature of the acid radicle. As has been shown, the acid value of the different hydrogen atoms differs when two or more are present in the same molecule, so that the acidity of such a solution may differ widely with different indicators. For general use, therefore, a strong acid should be chosen so that the strength of the solution may be the same with all indicators. A stable non-volatile acid is also desirable so that a solution once standardized may be permanent. These considerations limit us to the three commonly used strong acids, hydrochloric, sulphuric, and nitric. Of these three only the first two have found any very general use. The standardization of nitric acid offers some difficulties because it forms no insoluble weighable salt. It is also an oxidizing agent, so that titrations may be disturbed by secondary reactions. On the other hand, both sulphuric and hydrochloric acids are very stable and may also be precipitated and weighed with great accuracy. Choice must therefore be made between these two acids for a carefully standardized permanent acid to be used in the standardization of alkalies and other acids. For general use hydrochloric acid offers several decided advantages over sulphuric acid. It is appreciably stronger, so that the end-point with most indicators is considerably sharper than with sulphuric acid. This is partly due to the fact that there are two atoms of hydrogen in the sulphuric acid molecule, so that when the solution is partly neutralized an acid sulphate is formed whose hydrogen atom is not so strongly acid as the hydrogen atom first displaced. The use of sulphuric acid is also lim-

ited by the fact that it forms insoluble sulphates with the alkaline-earth metals. The gravimetric standardization of hydrochloric acid by precipitation as silver chloride is subject to fewer sources of error than the standardization of sulphuric acid by precipitation as barium sulphate.

353. Most Desirable Strength of Standard Acids.—Various strengths of acid are in use among chemists, many using tenth- or fifth-normal acids, while among commercial chemists the use of half- or full-normal solutions is quite common. The use of such concentrated solutions is defended by the argument that a sharp end-point may always be obtained with one drop of the acid. This is advantageous in commercial laboratories, where titrations must be made rapidly, and as large amounts of material must be weighed out to use a proper volume of acid, the weighings may be more quickly made. This is evident from the consideration that an error of 5 mg. on 5 grams is the same percentage as an error of 1 mg. on 1 gram. As methyl orange must frequently be used in the presence of carbon dioxide, the strong acid gives a sharp end-point even with one drop of the standard solution.

The use of the more dilute solutions is defended by the argument that a larger volume of the solution must be used for titrating a given weight of material, and therefore the reading of the volume on the burette is more accurate. The indefinite dilution of the solution does not lead to greater and greater accuracy, since a point is soon reached where a greater and greater volume of the solution must be taken to give a distinct end-point with the indicator. This limit is usually reached with fifth- or tenth-normal solutions. With moderate care a distinct end-point may be obtained even with methyl orange in the presence of carbon dioxide by means of one drop of fifth-normal acid. Another decided advantage of the fifth-normal acid is found in the moderately small coefficient of expansion with change in temperature, which with stronger acids becomes quite considerable. In general, therefore, more accurate work can be done with the more dilute acid, while time is saved at the expense of accuracy by the use of strong acids. The final decision must therefore be made on the requirements of the work at hand. For the exercises given in this book fifth-normal solutions will be uniformly used.

PROBLEM.

Problem 4. Calculate the number of grams of impure potassium carbonate which must be weighed out, so that when the solution is titrated with $N/5$ acid, the number of cubic centimeters used shall be equal to the per cent of potassium carbonate. Calculate the strength of acid in terms of normal to be made up, so that if 1 gram of impure potassium carbonate is weighed out, the per cent of potassium carbonate will be equal to the number of cubic centimeters used multiplied by two.

CHAPTER XXI.

STANDARD ACIDS.

STANDARDIZATION.

ONE of the most important points in volumetric work is the accurate standardization of the solutions. No subsequent care can overcome an error in this part of the work. Although many excellent methods of standardizing acids have been proposed, considerable skill and experience are necessary in order to secure absolutely reliable results.

354. Sodium Carbonate.—One of the oldest as well as most reliable methods of standardization is by means of sodium carbonate. It may be purchased in a high state of purity, so that it frequently needs only to be heated to completely dehydrate it and decompose any bicarbonate which may be present. For this purpose it need not be heated over 300° .* It is better to heat to this temperature than, as has long been the custom, to heat to dull redness and below the fusing-point of the carbonate, as small amounts of the carbonate are apt to be converted into the hydroxide by this treatment.

The carbonate must first be tested for impurities. It should dissolve completely in water. A portion of 2 or 3 grams is tested for chlorides by dissolving in water, acidifying with dilute nitric acid, and adding silver nitrate. Only a slight opalescence is permissible. Another 2- or 3-gram portion is dissolved in water, acidified with hydrochloric acid, and tested for sulphuric acid by means of barium chloride.

A very pure sodium carbonate may be obtained by heating PURE SODIUM BICARBONATE to 270° – 300° for one-half to one hour. The bicarbonate must be tested for impurities by the methods

* Lunge, *Zeit. f. angew. Chem.*, 1897, 522.

given for the carbonate. Small amounts of chlorides and sulphates may be washed out by repeated treatment with small amounts of cold distilled water. The bicarbonate may also be recrystallized. Distilled water heated to 80° in a Jena beaker is saturated with the bicarbonate by adding small amounts and stirring. The saturated solution is filtered through a folded filter in a hot-water funnel, and the solution cooled and vigorously stirred as the salt crystallizes out. It is filtered off in a funnel closed with a platinum cone or porcelain plate, washed with small portions of cold water and dried in a porcelain dish. Impure sodium carbonate may be purified by making a cold saturated solution, filtering if necessary, and saturating with carbon dioxide which has been washed by passing through a solution of sodium bicarbonate. The precipitated bicarbonate is filtered off and washed as already directed. It is advisable to preserve the bicarbonate as such and convert suitable portions into carbonate immediately before weighing it out for use. Better results will also be obtained if *separate small portions* are weighed out for each titration instead of making a standard solution, portions of which are measured out. The errors of the volumetric apparatus are thus avoided.

355. Crystallized Oxalic Acid.—Extended use has also been made of crystallized oxalic acid. A solution of an alkali, such as caustic soda or potash, is first standardized by means of the pure oxalic acid. The acid solution to be standardized is then carefully compared with the standardized alkaline solution. This method has the disadvantage that the errors of two titrations are introduced into the standardization. Carbon dioxide must also be absent as litmus or phenolphthalein must be used as the indicator.

Two difficulties are met with in preparing pure oxalic acid—the removal of traces of the alkalies and the drying of the crystallized product so as not to lose water of crystallization. The first object is attained by dissolving the commercial article in a mixture of equal parts of alcohol and ether, in which the alkali oxalates as well as other impurities are insoluble. After filtering the solution, the bulk of the alcohol and ether are distilled off, water is added, and the distillation continued. Finally the water solution is transferred to a porcelain dish and kept near the boiling-point until the last traces of the alcohol and ether as

well as any ethereal salts which may have been formed are volatilized. The steam will then have no odor. If the oxalic acid begins to crystallize out of the hot solution during this process, small quantities of distilled water are added from time to time. When the volatile matter has been expelled, the solution is allowed to cool with constant stirring. The crystals are filtered off in the usual manner and washed with small quantities of cold distilled water. They are then spread out on unglazed porcelain and exposed to the air until dry. The material is preserved in glass-stoppered bottles. The crystals must not be exposed to the air after they are dry, as shown by their non-adherence to a clean dry glass surface. The crystals then have the formula $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.

356. Anhydrous Oxalic Acid.—To obviate the uncertainty of the degree of hydration, anhydrous oxalic acid has been somewhat used. Drying at 60° to 80° for several hours is said to secure an anhydrous product. At 100° considerable oxalic acid is volatilized. As the anhydrous material is quite hygroscopic, it must be cooled in a desiccator and weighed as soon as cool. The pure recrystallized product prepared as already directed must be used for this purpose. Solutions of oxalic acid are not entirely stable, especially if dilute. For standardizing purposes it is therefore advisable to weigh out convenient amounts, and, after drying and weighing, to dissolve in water and titrate immediately.

357. Potassium Tetroxalate.—In place of the crystallized dehydrated oxalic acid, the use of crystallized potassium tetroxalate $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ has been recommended. This salt may easily be prepared by making a saturated solution of oxalic acid and filtering if necessary. One-fourth of this solution is neutralized with pure potassium carbonate and added with stirring to the remainder of the oxalic acid solution. The crystals which separate out are recrystallized from hot water several times and dried as directed for crystallized oxalic acid. The salt is preserved in well-stoppered bottles.

358. Potassium Dichromate.—The suggestion of Richter * to use pure potassium dichromate which may be titrated against a

* *Zeit. f. anal. Ch.*, 21. 205

solution of caustic potash, using phenolphthalein as the indicator, would seem to be of value. Potassium dichromate may readily be prepared pure and anhydrous.

359. Gravimetric Standardization.—The precipitation and gravimetric estimation of the acid radicle offers a most excellent method of standardizing acids, especially sulphuric and hydrochloric. The details of the precipitation and weighing of sulphuric acid as barium sulphate, and of hydrochloric acid as silver chloride, have already been given. A very simple gravimetric method consists in evaporating to dryness in a weighed platinum dish a measured volume of the acid solution which has been neutralized with ammonia. Both ammonium chloride and ammonium sulphate may be dried at 100° without appreciable volatilization. Very pure ammonia may be obtained for this purpose by distilling the concentrated solution and absorbing the gas in distilled water. Test-tubes may be used for this purpose, and the distilled ammonia should be used immediately. The weighed ammonium salt may be still further tested for impurities by volatilizing the weighed salt by gently heating the dish with the Bunsen burner and weighing the residue.

360. Standardization by Specific Gravity.—Standard solutions of acids, especially sulphuric acid, may be made with almost as high a degree of accuracy as by the methods already given, by carefully taking the specific gravity of the concentrated acid and diluting a measured or weighed amount to a definite volume. The C. P. concentrated sulphuric acid should first be diluted to about 30%. Acid of this concentration is not hygroscopic, and the change in specific gravity with change in concentration is greater than with the stronger acid. The specific gravity is carefully taken at the standard temperature, 15° C., by means of a Westphal balance or carefully calibrated pycnometer. The greatest care should be taken to bring the temperature to exactly 15° C. with a tested thermometer. If the acid is to be measured out it must be kept at this temperature as carefully as when the specific gravity is being taken. This difficulty may be obviated by weighing the acid. This method has the additional advantage that the weight can be taken far more accurately than the volume, especially if it is corrected for air displacement. The weighing

need not be made closer than a few milligrams, as an error of 10 mg. is negligible. The calculation is also very simple. The number of grams of acid required per liter for the solution to be made is divided by the percentage given in the table for the specific gravity found. The quotient multiplied by 100 is the number of grams of the concentrated acid to be weighed out and diluted to a liter.

As the measuring out of concentrated hydrochloric acid is accompanied by much more uncertainty, it is advisable to measure out a little more of this acid than the calculated amount, so that after standardization it may be diluted to the exact strength. A solution of hydrochloric acid of approximately constant strength may be obtained by boiling either the dilute or concentrated acid. Equilibrium is soon reached so that, when boiling at about 760-mm. pressure, both acid and water are volatilized in equal amount from the residue, which contains 20.2% of hydrochloric acid and has a specific gravity of 1.10.* 180 grams of this acid diluted to 1 liter give an acid slightly stronger than normal.

361. Dilution of Acid to Exact Strength.—If the sulphuric acid is not made by diluting a strong acid whose specific gravity has been very carefully taken, it should also be made so as to be somewhat stronger than the acid required. At least $1\frac{1}{2}$ liters should be made, placed in a bottle of suitable size and well mixed by shaking. After carefully standardizing the acid by two of the methods already given, it should be diluted to the exact strength. Perhaps the simplest method of calculating the results of each standardization is to find the number of grams of acid present per liter. The average of the standardizations, which agree within at least 0.2%, is taken and divided into the number of grams per liter required. For normal hydrochloric this will be 36.46 grams and for normal sulphuric 49.04 grams. The quotient multiplied by 1000 gives the number of cubic centimeters to be diluted to 1 liter. This number subtracted from 1000 gives the number of cubic centimeters of water to be measured out into the liter-flask, which is then filled to the mark with the acid to be diluted. The strength of the diluted acid is verified

* Roscoe and Dittmar, Jour. Chem. Soc., XII, 128, 1860.

by one of the methods already used. This is especially necessary if the amount of water added per liter is large. Frequently the most satisfactory method of standardization is by the use of sodium carbonate, this being a volumetric method, and is carried out under the same conditions that will be met in regular work.

EXERCISE 48.

Preparation of Standard N/5 Hydrochloric Acid.

To 75 c.c. of concentrated hydrochloric acid an equal volume of water is added and the solution boiled in a beaker or a porcelain dish for a few minutes. About 36 grams of this acid are weighed out and transferred to the liter flask, which should be clean, but need not be dry. The beaker or other vessel is rinsed out into the flask. Distilled water is added until the flask is filled to the mark. The solution is poured into a large bottle,* which, if not dry, should first be rinsed with a little of the acid. The flask is rinsed with a little distilled water, and a second liter of acid made and poured into the large bottle. The bottle is filled from a third liter of the diluted acid. After thoroughly mixing the solution by shaking, the acid is standardized by two of the following methods, duplicate determinations being made by each method.

STANDARDIZATION.

362. First Method. By Evaporation with Ammonia.—Measure out with a burette or a calibrated pipette 50 c.c. of the acid into a weighed platinum dish. Fit a small flask or a test-tube with a glass delivery-tube bent twice at right angles. Place 10 to 15 c.c. of strong ammonia in the flask and distil off the ammonia, using a small flask or test-tube containing 15 to 20 c.c. distilled water as a receiver. The end of the delivery-tube should dip into the distilled water. Neutralize the acid with this ammonia, evaporate to dryness on the water-bath, and weigh the ammonium chloride. Bring to constant weight by heating on the water-bath for fifteen to twenty minutes and weighing. When the weight is constant volatilize the ammonium chloride by gently heating the dish with the Bunsen burner, and weigh again. Deduct this weight from the weight of the dish and the residue dried on the water-bath to obtain the weight of the ammonium chloride.

Calculate the weight of hydrochloric acid present in 50 c.c. by the proportion,

$$\text{Mol. wt. NH}_4\text{Cl} : \text{Mol. wt. HCl} :: \text{weight NH}_4\text{Cl} : \text{weight HCl}.$$

* The 2½-liter glass-stoppered bottles in which the concentrated C. P. acids are purchased are very convenient for this purpose.

363. Second Method. By Titration with Sodium Carbonate.—Place about 4½ grams of pure sodium bicarbonate in a weighed platinum crucible. Place it in a sand-bath so that the crucible is nearly immersed in the sand. Insert a thermometer in the bicarbonate and heat the sand-bath until the thermometer registers 270° to 300° for one-half to one hour. If an air-bath is at hand which can be raised to this temperature, the bicarbonate may be heated in it for the same length of time. It may then be placed on a weighed watch-crystal. The carbonate is cooled in the desiccator and weighed. The heating is repeated for half-hour periods until constant weight is obtained. The weight of the carbonate is then brought to exactly 2.650 grams by taking out small portions with a spatula. Transfer the carbonate to a beaker, rinse the crucible with water, dissolve the material in water, and transfer to a 250-c.c. flask. After diluting to the mark and shaking thoroughly, fill a burette with the solution and titrate against the hydrochloric acid solution, using methyl orange as the indicator. *The titration should be made the same day the carbonate is dissolved, as the solution is not entirely stable because of action on the glass.*

Measure out 25 c.c. of the alkaline solution into a 100-c.c. beaker, and add one drop of the indicator. 50 c.c. of distilled water are placed in a similar beaker, one drop of methyl orange added, and the solution saturated with carbon dioxide which has been passed through a solution of sodium bicarbonate. To the beaker containing the alkali hydrochloric acid is added until, when compared with the neutral solution, a pink tinge is noticeable. A drop of alkali is then added, and if the neutral tint is not restored, the solution is made alkaline and again neutralized by cautious additions of the acid. This process is repeated until no difficulty is experienced in so closely judging the acid tint that one drop of the alkali will restore the neutral tint. When a satisfactory end-point has been obtained both burettes are carefully read. The titration is repeated until duplicates agreeing within less than 0.1 c.c. are obtained.

When skill has been attained in making the titration, more accurate results can be obtained by weighing out portions of the carbonate just sufficient for one titration. A considerable amount of the bicarbonate is converted into carbonate and brought to constant weight. Portions weighing from 0.4 gram to not over .5265 gram are weighed out and transferred to beakers. After dissolving in about 50 c.c. of distilled water and adding a drop of methyl orange the solutions are titrated with the hydrochloric acid.

Calculation.—By dividing the weight of sodium carbonate by the number of cubic centimeters of acid used in each case the weight of sodium carbonate per cubic centimeter will be obtained, which for an exactly N/5 normal solution is .01061 gram. The amount found per cubic centimeter should be divided into .01061, and the quotient multiplied by 1000 to find the number of cubic centimeters to be diluted to one liter to make the acid exactly fifth-normal.

364. Third Method. By Determination of Chlorine as Silver Chloride.—Prepare two Gooch crucibles and dry on the hot plate. Measure out two 25-c.c. portions of the acid into Erlenmeyer flasks and dilute to 200 c.c. Add silver nitrate solution with constant agitation until all the chlorine is precipitated. Heat nearly to boiling, and shake vigorously until the supernatant liquid is clear. Decant the clear liquid through the Gooch crucibles, wash two or three times by decantation with hot water, transfer the precipitates to the crucibles, and wash with hot water until free from silver. Dry on the hot plate and weigh. If the duplicates differ from each other by more than 1 mg., repeat the determination, using the same crucibles without removing the precipitates.

Calculation and Dilution of Acid.—From the average weight of silver chloride obtained from 25 c.c. of acid the strength of the acid is obtained by the following proportion:

$$\text{Mol. wt. AgCl} : \text{mol. wt. HCl} :: \text{weight AgCl} : X,$$

where X is equal to the number of grams of hydrochloric acid in 25 c.c. This number divided into 7.292 and the quotient multiplied by 25 $\left[\frac{7.292}{40X}(1000) \right]$ gives the number of cubic centimeters to be diluted to 1000 to give a fifth-normal solution. This number subtracted from 1000 gives the number of cubic centimeters of water required. If the liter-flask is wet, it should be rinsed two or three times with a little of the acid to be diluted. The necessary amount of water is carefully measured out with a burette and allowed to flow into the flask, which is then filled to the mark with the acid and thoroughly shaken. The diluted acid is emptied into a bottle capable of holding all of the acid to be diluted. If it is not dry, it is rinsed with a little of the diluted acid. The remainder of the acid is diluted in the same manner and poured into the large bottle. The strength of the diluted acid must be verified by one of the methods already used. This is especially necessary if the amount of water added is large.

DETERMINATION OF SODIUM HYDROXIDE, CARBONATE, AND BICARBONATE.

These three compounds of sodium evidently cannot occur together, because the hydroxide and bicarbonate would react to form the normal carbonate. We have therefore to consider the determination of *sodium hydroxide* and *carbonate* when occurring together, as well as the analysis of mixtures of the *bicarbonate* and the *carbonate*.

365. Titration of Carbonic Acid.—One method of analyzing the first combination has already been outlined in the discussion

of the properties of indicators. Using phenolphthalein as the indicator, all of the hydroxide will be neutralized by standard acid, while the carbonate will be converted into bicarbonate. On adding methyl orange and continuing the addition of acid until the solution is pink the bicarbonate formed will be decomposed. The amount of acid added during the second part of the titration will be half that required to completely decompose the carbonate. The difference between the two amounts of acid used will be the amount necessary to neutralize the sodium hydroxide. This method will give correct results only if the *amount of carbonate is small and the solution is dilute and cold*. The escape of carbon dioxide because of a local excess of acid must be absolutely prevented by vigorous stirring. The method is well adapted to the analysis of commercial caustic soda.

366. Precipitation of Carbonic Acid.—If a large amount of sodium carbonate is present, the total amount of alkali present is determined by titration with standard acid, using methyl orange as the indicator. From another portion the carbon dioxide is precipitated by the addition of BARIUM CHLORIDE solution. The alkali is in this manner converted into chloride, and on titrating the solution only the alkali hydroxide remains to react with the acid. Any excess of barium chloride will remain as such or react with the sodium hydroxide, giving sodium chloride and barium hydroxide. It has been shown, however, that the excess of barium chloride must be small, as otherwise the percentage of caustic soda found will be low. Using phenolphthalein as the indicator, the alkali hydroxide may be titrated in the presence of the barium carbonate, if care is exercised to stir the solution thoroughly so as not to have, at any time, an excess of acid present in any part of the solution. The acid reaction of the solution is not permanent because of the slight solubility of the barium carbonate. The titration is therefore conducted quite rapidly and a momentary disappearance of the red color is taken as the end-point.

The solution, after the addition of the barium chloride, may also be diluted to a definite volume, and after allowing the precipitate to settle, a measured portion of the clear liquid may be withdrawn and titrated. The amount of acid necessary to neu-

tralize the carbonate present is found by subtracting the amount of acid necessary to neutralize the sodium hydroxide from the amount used in titrating the total alkali.

367. Determination of Bicarbonates.—If a mixture of sodium carbonate and bicarbonate is to be analyzed, the total alkali may be found by titration with acid, using methyl orange as the indicator. As the precipitation of the carbon dioxide by barium chloride would tend to produce free acid according to the equation



thus preventing the completion of the reaction, a measured excess of standard alkali solution must first be added. After the precipitation of the carbon dioxide by the addition of barium chloride the alkali present is titrated with standard acid. The difference between the amount of alkali added and that found after the precipitation of the carbon dioxide is that necessary to convert the bicarbonate present into carbonate or to neutralize the equivalent amount of hydrochloric acid liberated from the barium chloride. The standard alkali used in this case may be either ammonia or caustic soda. The former is disadvantageous because of its disturbing effect on phenolphthalein, while it is difficult to obtain either alkaline solution free from carbon dioxide. Perhaps the simplest way of overcoming this difficulty is to conduct a blank determination by precipitating the carbonate from a measured volume of the alkaline solution and titrating as in the actual determination.

EXERCISE 49.

Determination of Sodium Hydroxide, Sodium Carbonate, and Water in Caustic Soda.

Weigh out in a weighing-bottle from 3 to 5 grams of caustic soda. Do not take the sample from the top of the bottle, where it has been exposed to the moisture and carbon dioxide of the air. Transfer to the weighing-bottle with as little exposure as possible and stopper quickly. When weighed, transfer to a beaker, rinse the bottle with water, and dissolve the soda. Transfer to a 250-c.c. flask and dilute to the mark with boiled water.

368. First Method. Titration of the Carbonic Acid.—Take out 25 c.c. with a pipette and dilute to about 100 c.c. with boiled water which has been thoroughly cooled. Titrate, while stirring vigorously, with $N/5$ acid after adding 2 or 3 drops of phenolphthalein until the pink color has just disappeared.

Add 1 or 2 drops of methyl orange and continue the titration until a faint pink appears. Repeat until duplicates are obtained. Twice the amount of acid used in the methyl-orange titration is the amount necessary to neutralize the sodium carbonate. 1 c.c. of N/5 acid equals .01061 gram Na_2CO_3 . The difference between the amounts of acid used in the phenolphthalein and the methyl orange titrations is the amount necessary to neutralize the sodium hydroxide. 1 c.c. of N/5 acid equals .008012 gram NaOH. Calculate the amount of Na_2CO_3 and of NaOH present in 250 c.c. The difference between the sum of these weights and the weight of the caustic soda gives the weight of water present. Calculate the per cent of each constituent.

369. Second Method. Precipitation of the Carbonic Acid.—Measure out 25 c.c. of the soda solution with a pipette into a beaker, add 1 or 2 drops of methyl orange, and titrate to faint pink with N/5 acid.

Measure out 50 c.c. into a 100-c.c. flask and add with shaking a little dilute solution of barium chloride drop by drop as long as a white precipitate forms. Dilute to the mark with boiled and cooled water, shake thoroughly, and allow to settle. Measure out 50 c.c. and titrate with the N/5 acid, using phenolphthalein as the indicator. Repeat both titrations until duplicates are obtained. The second titration gives the amount of acid necessary to neutralize the caustic soda, while the difference between the first and second gives the amount of acid necessary to neutralize the sodium carbonate present in 50 c.c. of the solution. Calculate the percentage of NaOH, Na_2CO_3 , and H_2O as directed under the first method.

DETERMINATION OF HARDNESS OF WATER.

370. Temporary Hardness or Alkalinity.—The hardness of water is caused by the presence of salts of calcium and magnesium in solution. If these metals are in solution as bicarbonates, they may be precipitated as carbonates by boiling the water, the excess of the carbon dioxide being expelled. The hardness of water which may be removed in this manner is called temporary hardness. The amount of calcium and magnesium held in solution in this manner may be ascertained by titrating the solution with a standard acid, using methyl orange or erythrosene and chloroform as the indicator. The result is given in parts of calcium carbonate per 100,000, giving the so-called *degrees of hardness*. As the bicarbonates of calcium and magnesium react alkaline to methyl orange and some other indicators, this titration also gives the *alkalinity* of the water. If sodium or potassium carbonates are present, they will also react alkaline, but a correction for this error will be obtained in determining permanent hardness.

371. Permanent Hardness or Incrustants.—The presence of *chlorides* and *sulphates* of *calcium* and *magnesium* produce permanent hardness, so called because these salts cannot be removed by boiling the water. On adding excess of sodium carbonate and evaporating to dryness, the sulphates and chlorides of calcium and magnesium are converted into the carbonates of these two metals and the sulphate and chloride of sodium. The bicarbonates of calcium and magnesium are also decomposed. On filtering and washing, the carbonates of calcium and magnesium, being insoluble, remain on the paper, while the excess of the sodium carbonate as well as the sodium chloride and sulphate pass into solution. The excess of sodium carbonate having been ascertained by titration, the amount needed to decompose the chlorides and sulphates of calcium and magnesium is found by difference. If the so-called *soda reagent* is used, the magnesium will be precipitated as hydroxide. The amount of permanent hardness is also calculated as parts of calcium carbonate per 100,000 or per million. As the principal salt producing permanent hardness is calcium sulphate, which tends to produce a very hard scale in boilers, the term *incrustants* is also used to designate these constituents of the water. If the alkalinity of the filtrate is greater than that due to the sodium carbonate added, alkali carbonates must have been present in the water. Permanent hardness is then absent, and the amount of alkali carbonates present computed as calcium carbonate must be subtracted from the temporary hardness already found.

EXERCISE 50.

Determination of Hardness of Water, Temporary and Permanent.

Make an N/50 solution of hydrochloric acid by measuring out 100 c.c. of the N 5 acid into a liter flask and diluting to the mark. Make an N/50 solution of sodium carbonate by diluting 100 c.c. of the N/5 alkali to a liter, or weigh out 1.061 grams of the pure dry salt, dissolve in water, and make up to a liter.

372. Temporary Hardness or Alkalinity.—Measure out 100 c.c. of the water to be tested into a porcelain dish and add one drop of methyl orange. Measure out 100 c.c. of distilled water into a similar porcelain dish and add one drop of the indicator. Add the N/50 acid drop by drop until a faint pink color is obtained. Titrate the water in the other dish with the acid until the color matches that in the dish containing the distilled water. From the amount of acid used, less the amount added to the distilled water (.1 to

.3 c.c.), the alkalinity or hardness is calculated in parts per 100,000 or parts per million.

Erythrosene and chloroform may also be used as the indicator in this titration. The end-point with this indicator is sharper and its use is especially to be advised when alum is likely to be present in the water. 0.1 gram of the erythrosene is dissolved in 1000 c.c. of water. 100 c.c. of the water to be tested is placed in a 250-c.c. glass-stoppered bottle: 2.5 c.c. of the indicator* and 5 c.c. of chloroform are added. The bottle is shaken thoroughly, so that the chloroform forms an emulsion. The standard acid is added and the shaking continued until the color is discharged. The alkalinity is calculated from the amount of acid used.

373. Permanent Hardness or Incrustants.—100 c.c. of the water is measured out into a porcelain evaporating-dish. Add a measured amount of the N/50 sodium carbonate solution sufficient to make the water strongly alkaline. Evaporate to dryness, take up with a small amount of water, filter, and wash the dish and filter-paper until free from alkali. Titrate the excess of the alkali with N/50 acid, using methyl orange as the indicator. The difference between the amount of alkali added and that titrated back is the amount used in precipitating the calcium and magnesium, which produced the permanent hardness. The calculation is made in the same manner as that of temporary hardness. If the amount of alkali titrated back should be greater than the amount added, the water contains alkali carbonates which have been reckoned as temporary hardness. The amount of excess should therefore be deducted from the temporary hardness. Permanent hardness is absent.

The so-called *soda reagent* gives somewhat more accurate results because the salts of calcium and magnesium are rendered less soluble by this reagent. It is composed of equal parts of N/10 sodium carbonate and sodium hydroxide. It may be prepared by weighing out 2.653 grams of pure sodium carbonate or measuring out 250 c.c. of N/5 sodium carbonate solution and 250 c.c. of N/5 sodium hydroxide solution (page 282), and diluting to one liter. 200 c.c. of the water to be tested is measured into a Jena Erlenmeyer flask. After boiling 10 minutes to expel free carbonic acid, 25 c.c. of the soda reagent is added. It is again boiled down to a volume of 100 c.c., cooled and rinsed into a 200-c.c. graduated flask and the volume made up to 200 c.c. with boiled distilled water and thoroughly mixed by shaking the flask. The solution is filtered through a dry paper, and after rejecting the first 50 c.c., 100 c.c. is titrated with the N/50 acid, using erythrosene as the indicator. The calculation is made in the same manner as before except that the 25 c.c. of tenth, normal soda reagent must be considered equal to 125 c.c. of the N/50 acid.

When the permanent hardness is small, better results are obtained by determining total hardness by means of the soda reagent, and getting per-

* When erythrosene is referred to as the indicator, the .01% solution of the sodium salt of erythrosene is implied.

manent hardness by difference. For this purpose the exact amount of acid used in titrating the alkalinity is added to 100 c.c. of the water being tested, thus converting the temporary hardness to permanent hardness, which is determined by the method already described.

EXERCISE 51.

Standard N/5 Sulphuric Acid.

374. Specific Gravity.—To 100 c.c. distilled water add 40 grams concentrated sulphuric acid. Cool to 15° C. and take the specific gravity with the Westphal balance. In setting up this balance, the screw *A* is adjusted so that the two points at *C* are exactly on a level when the thermometer *D*

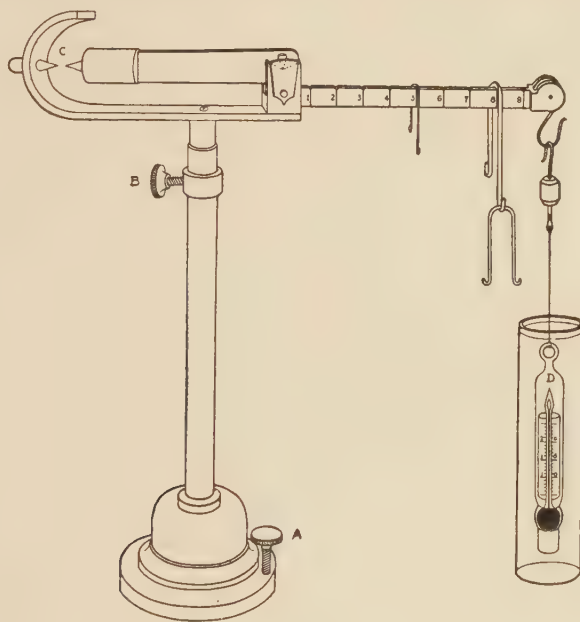


FIG. 45.

is suspended in the air. By the thumb-screw *B* the height of the beam is regulated so that the thermometer does not touch the bottom of the small cylinder. The weights are of four sizes. The largest size hung on the hook on the end of the beam gives units, while on any other space gives tenths, the next size gives hundredths, the next size thousandths, and the smallest ten-thousandths of specific gravity. The instrument in Fig. 45 reads 0.0885, the largest size weight being absent. The sulphuric acid is poured into the cylinder and the weights placed on the various divisions until the two points at *C* are again exactly on a level. If the thermometer now reads 15°, the

specific gravity is given by the weights on the beam. The percentage of H_2SO_4 , corresponding to the specific gravity found, is obtained from the table of specific gravity of sulphuric acid given on p. 523. The specific gravity times the per cent of H_2SO_4 present gives the number of grams of H_2SO_4 per cubic centimeter. The number of cubic centimeters of acid to be measured out to give 9.808 grams of H_2SO_4 is now computed. The acid, still being at 15° , is transferred to a burette, measured out into a liter flask, diluted to the mark and thoroughly mixed. Another liter is prepared in the same manner and mixed with the first in a 2-liter bottle. Instead of measuring out the concentrated acid, it may be weighed out. For this purpose it need not be kept at 15° . The amount to be weighed out for one liter is found by dividing 9.808 by the per cent found in the table and multiplying the quotient by 100. If this solution has been carefully prepared, it will be very near the calculated strength.

STANDARDIZATION.

First Method.—Same as first method in Exercise 48.

Second Method.—Same as second method in Exercise 48.

375. Third Method. Precipitation as Barium Sulphate.—Measure out by a burette 50 c.c. of the sulphuric acid into a beaker. Dilute to 400 c.c., heat to boiling, and add barium chloride solution drop by drop while stirring the solution vigorously until all of the sulphuric acid is precipitated. Digest until the solution is clear. Wash by decantation, dry, ignite, and weigh. Repeat the determination until duplicates are obtained agreeing within .2%. Compute the weight of H_2SO_4 , multiply by 20, and divide 9.808 by the product. This gives the number of cubic centimeters of the acid to be diluted to 1000 c.c. The acid is diluted as directed in Exercise 48.

DETERMINATION OF SPECIFIC GRAVITY.

The strength of acids as well as of a great variety of solutions is commonly ascertained by a determination of the specific gravity. This method is especially advantageous when dealing with solutions of pure substances.

376. Specific Gravity may be defined as the ratio between the weight of a given volume of a substance and the weight of an equal volume of some standard substance. When dealing with liquids or solids, water is almost invariably used as the standard of comparison. In terms of the metric system of weights and measures, specific gravity may be defined as the ratio of the weight of a cubic centimeter of a substance to the weight of a cubic centimeter of water. As the weight of the latter is 1 gram, specific

gravity may be defined as the weight in grams of 1 cubic centimeter of a given substance. When using the metric system of weights and measures, specific gravity is therefore identical with density, which is defined as the weight of unit volume of a substance.

377. Standard Temperatures.—With the English units of weights and measures, specific gravity and density are not identical. The identity is not exact even with the metric system, except when the water is used at its maximum density (4° C.) and is weighed in vacuo. Considerable confusion has arisen because in determining specific gravity the weight of water in the air and at other temperatures than 4° C. has been assumed to be 1 gram per cubic centimeter. Even when the exact weight of the water has been ascertained, confusion may arise if the conditions used are not given. The temperature at which both the substance and the water are weighed should always be given. This is ordinarily done by placing a fraction after the figure giving the specific gravity. The numerator of the fraction gives the temperature of the substance, while the denominator gives the temperature of the water. $1.563\frac{15}{4}$, for instance, means that a given volume of the substance at 15° weighs 1.563 times as much as the same volume of water at 4° C. If these weights have been reduced to vacuo, we may also state that the density of the substance at 15° is 1.563; that is, the weight of 1 cubic centimeter is 1.563 grams. For substances whose specific gravity is small, the correction obtained by reducing the weight to vacuo is very small, being about one-tenth per cent. The error introduced by considering the weight of 1 c.c. of water at 15° to be 1 gram is .08%, while at 20° the error is .17%, and at 25° it is .29%. As both of these corrections are positive, the error introduced by neglecting both of them is the sum of the two. The simplest and most convenient method of determining specific gravity consists in weighing both the substance and the water in the air at ordinary temperatures, such as 15° or 20° . When the specific-gravity tables have been calculated from determinations made in the same manner, no error is introduced unless the volume of solutions are calculated from their weight or weights from volumes. Such calculations require true densities.

378. Pycnometers.—The most reliable method of determining specific gravity involves the use of some form of pycnometer. The simplest form of this instrument consists of a small bottle closed with a glass stopper containing a capillary opening through which the excess of liquid may escape when inserting the stopper after filling the bottle. It is first weighed empty and dry, again weighed after filling with water, and finally the weight of the bottle filled with the substance being tested is taken. The latter as well as the water must be brought to the standard temperature before filling the bottle. As most liquids transmit heat quite readily and have a fairly high coefficient of expansion, there is considerable difficulty in getting the pycnometer filled at the desired temperature. After being filled the bottle may be placed in a vessel of water which is maintained at the standard temperature. If allowed to remain sufficiently long in the water, the bottle and contents ultimately attain the same temperature as the water. The time necessary for this purpose varies with the viscosity and other properties of the liquid. To obviate uncertainty in this respect, pycnometers are made with a thermometer ground so as to serve as a stopper, the bulb being in the liquid while the stem projects out of the bottle. A capillary tube is fused into the side of the pycnometer and is provided with a hollow glass ground cap. The liquid is cooled down below the standard temperature before filling the bottle, which is then placed in water maintained at this temperature. As the liquid expands the excess escapes through the capillary tube. When the thermometer in the pycnometer indicates the desired temperature, the excess of liquid on the end of the capillary tube is removed and the cap put on. The bottle is removed from the water and wiped clean and set aside until the contents have reached room temperature, when it is weighed. The weight of distilled water which just fills the bottle at the standard temperature is obtained in the same manner. If the true density is desired, the weight of the water is corrected for air displacement, as explained on page 11, and the volume in cubic centimeters calculated from the density of the water at the temperature used. The weight of an equal volume of water in grams at 4° C. in vacuo is numerically equal to the number of cubic centimeters found by the calculation given. This weight,

divided into the weight of the bottle full of the liquid being tested, gives the density or the specific gravity compared with water at 4° C.

379. The Westphal Balance.—The manipulation of this instrument is very simple, and the results are almost as accurate and reliable as those obtained with the pycnometer. It consists of a beam suspended on a knife-edge and so adjusted that when a glass plummet is suspended from a hook at one end, the weight on the other end is just counterbalanced, as indicated by the two points at *C*, Fig. 45, which are then exactly on a level. If they are not, the balance may be adjusted by means of the thumb-screw *A*. As commonly made, the plummet weighs 15 grams and displaces 5 grams of water at the standard temperature. The arm from which the plummet is suspended is divided into 10 equal divisions, and a set of weights in the form of riders is provided, such that the largest is just equal to the weight of the water displaced by the plummet, generally 5 grams. If the plummet is suspended in water, it will lose 5 grams in weight, which will be exactly counterbalanced by the large weight when hung from the hook at the end of the beam. This indicates a specific gravity of one. When the plummet is suspended in other liquids, the large weight indicates tenths when placed on other divisions of the beam. Similarly, riders weighing 0.5, 0.05, and 0.005 gram indicate hundredths, thousandths, and ten thousandths of specific gravity when they are hung on the beam so as to counterbalance the buoyant force of the liquid being tested on the glass plummet. The temperature of the liquid is taken by means of a thermometer within the plummet.

380. Hydrometers, or specific-gravity spindles, are instruments the construction of which is based on the principle that the buoyant force of a liquid is directly proportional to its density or specific gravity. The hydrometer is essentially a long, closed, glass tube, more or less enlarged at the lower end and so weighted with shot or mercury that it will assume a perpendicular position in a liquid in which it does not entirely sink. As the weight of the instrument is constant, the depth to which the hydrometer sinks in a given liquid may be used as an index of the specific gravity of the liquid. A paper scale is inserted in the stem of the instru-

ment and fixed in such a position that the specific gravity may be read directly on the scale at the surface of the liquid. A thermometer is sometimes made a part of the instrument, so that the temperature at which the readings are taken may be noted. These instruments are very convenient and rapid in use, but are not well adapted for accurate work. Specific gravity is often designated by degrees of one of the several scales which have been devised and which are almost invariably made use of in the construction and graduation of hydrometers. The degrees Twaddell are the simplest and most scientific of these scales. On this scale a degree corresponds to .005 specific gravity above unity. 7° Twaddell is therefore equal to 1.035 sp. gr.; 30° is equal to 1.150, etc. The spindle is usually made quite large, with a very small stem, so that determinations of specific gravity may be made with very great accuracy. The entire scale of 150° is usually divided equally among 6 spindles. This instrument is very generally used in Great Britain.

381. The Baumé Scale is generally used in other countries. This instrument was originally graduated as follows: The point to which the spindle sank in water at 17½° C. was marked 0, and the point to which it sank in a 10 per cent solution of common salt was marked 10°. This space was divided into 10 equal divisions, and the remainder of the stem marked off in spaces of the same length. This gave the scale for liquids heavier than water. For liquids lighter than water, the point to which the spindle sank in a solution of 1 part of salt in 9 parts of water was marked 0, and the point to which it sank in water was marked 10. One-tenth of this space was taken as a degree, and the remainder of the scale divided into degrees of this size. This method gave degrees of unequal value in terms of specific gravity. On account of the varying purity of the salt used, the degrees on different instruments varied greatly in value, so that 66° Baumé might indicate in the case of sulphuric acid a minimum strength of 89.5% H_2SO_4 , or a maximum of 95% H_2SO_4 . As a remedy for this confusion, several formulas have been proposed by which the degree Baumé may be calculated from the specific gravity, or the latter calculated from the former. The so-called rational formula is $d = \frac{144.3}{144.3 - B^\circ}$, in which d = specific gravity and B° = the degree

Baumé. In Holland the formula $d = \frac{144}{144 - B^\circ}$ and in the United States the formula $d = \frac{145}{145 - B^\circ}$ has been adopted as the standard Baumé scale for liquids heavier than water, and for liquids lighter than water, the formula $d = \frac{140}{130 + B^\circ}$ has been adopted as the standard American scale. Under these circumstances it is evident that the Baumé scale is the worst which could have been adopted, and that degrees Baumé is by no means a definite statement of specific gravity unless it is known what particular scale has been used. The formula giving the relation between specific gravity and degrees Baumé should be printed on the scale, and only the standard American scale should be used in the United States.

PROBLEMS.

Problem 5. How many cubic centimeters of sulphuric acid having a specific gravity of 1.3567 at 15° must be diluted to a liter to make N/5 acid? How many grams of the same acid must be used for making a liter of N/5 acid?

Problem 6. Four grams of caustic soda were weighed out, dissolved in water, and diluted to 500 c.c. Fifty c.c. of this solution required, when titrated with N/5 acid and phenolphthalein, 46.36 c.c. of acid, and when methyl orange was added, 0.94 c.c. was required to give the end-point with this indicator. Calculate the percentage of sodium hydroxide, sodium carbonate, and water in the caustic soda.

Problem 7. One gram of sodium phosphate was dissolved in water and titrated with N/5 acid, using phenolphthalein as the indicator, 0.67 c.c. of the acid being used. Methyl orange was then introduced and acid again added until the end-point was reached, 13.92 c.c. of the N/5 acid being used in the second titration. Calculate the percentage of crystallized trisodium and disodium phosphate present.

Problem 8. Ten grams of a mixture of sodium carbonate and sodium bicarbonate was dissolved in water and diluted to a liter. To 50 c.c. of this solution, 25 c.c. of N/5 sodium hydroxide was added, and then enough barium chloride to precipitate the carbonate. On titrating with N/5 hydrochloric acid, 15 c.c. was used. Another 50-c.c. portion required 40 c.c. when titrated with the N/5 acid and methyl orange. Calculate the percentage of sodium carbonate and bicarbonate present.

Problem 9. In titrating 100 c.c. of a sample of water, 5 c.c. of N/20 sodium hydroxide was required with phenolphthalein. Another 100-c.c.

portion required 15 c.c. of N/20 hydrochloric acid with methyl orange. Calculate (a) the amount of carbon dioxide present and the alkalinity in parts per million; (b) calculate the amount of calcium oxide necessary to soften 1000 gallons of the water; (c) calculate the amount of lime-water necessary to soften the same quantity of water.

Problem 10. To 100 c.c. of the same water, 50 c.c. of N/50 sodium-carbonate solution was added, and after evaporation, 35 c.c. of N/50 hydrochloric acid was required to titrate the excess. Calculate (a) the permanent hardness in parts per million; (b) the amount of sodium carbonate necessary to soften 1000 gallons of the water.

After adding the softening agent and allowing the water to settle, or filtering it, how could (a) the presence of an excess of lime be found by titration, (b) a deficiency of lime, (c) an excess or deficiency of the soda-ash?

CHAPTER XXII.

STANDARD ALKALIES.

382. Standard Alkaline Solutions not Permanent.—While standard solutions of hydrochloric and sulphuric acids may be kept for months and even years without change in strength, no suitable alkaline solution has been found which in practice may be preserved without deterioration. This arises mainly from two causes, the *absorption of carbon dioxide* from the air and the *action of the alkaline solutions on the glass* of the containing bottles. In the case of AMMONIA neither of these causes of deterioration is serious, but another difficulty is met with in the volatility of the base. Moreover, it is a weak base and cannot be used with phenolphthalein. The strength of all basic solutions must therefore be frequently checked by titration with standard acid. The presence of carbon dioxide may in many cases be disregarded by using methyl orange as the indicator in titrations. As this is not always possible on account of the nature of the acid, standard alkaline solutions must frequently be prepared and kept free from carbon dioxide by methods described later.

383. Caustic Soda has been found to be the alkali best suited for general work. It is a strong base, forms soluble salts with all acids, and may be prepared of any desired strength, while the pure commercial article is cheaper than caustic potash. A solution of the highest purity may be made by dissolving metallic sodium in pure water. This metal may now be readily obtained in pure condition. Caustic soda made from the metal may also be purchased. The pure commercial caustic soda almost invariably contains small amounts of chlorides, sulphates, silica, and alumina, besides considerable amounts of carbon dioxide and water. About 20% more than the calculated amount of NaOH should therefore be weighed out, and dissolved in the required

amount of water. After titrating this solution against standard acid it is diluted to the required strength. On account of the presence of carbon dioxide, methyl orange must be used as the indicator, or litmus accompanied by boiling to expel the carbon dioxide.

384. Removal of Carbon Dioxide.—The alkaline solution must be kept in a bottle closed with a rubber stopper or a glass stopper coated with paraffine or vaseline. If the solution is to be used for titrating organic acids with phenolphthalein as the indicator, the carbon dioxide must be removed by means of *barium chloride* or *hydroxide*, and the solution subsequently protected from the carbon dioxide of the air. This may be accomplished either by pouring a layer of kerosene over the solution or by passing the air which enters the bottle through a soda-line tube. In either case the soda solution must be withdrawn by means of a siphon. The arrangement shown in Fig. 46 is very convenient. The caus-

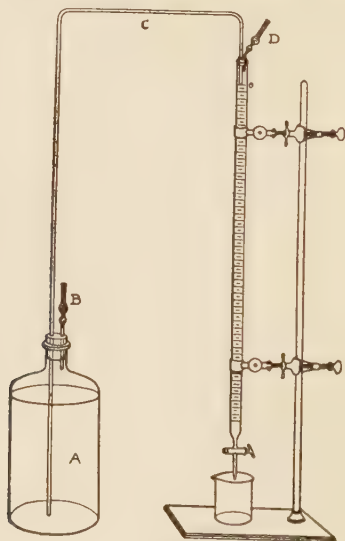


FIG. 46.

tic-soda solution is made up in a bottle of suitable size and, after the addition of enough barium chloride or barium hydroxide solution to precipitate all of the carbon dioxide, is allowed to stand until the precipitate has settled. The clear solution is then siphoned off into the bottle *A*, and if a layer of petroleum-oil is not

placed on top, the tube *B* is filled with soda-lime and inserted into the stopper. The long arm of the siphon *C* is pushed through the second hole of the stopper so that a space of about one inch is left between the end and the bottom of the bottle. The alkali may then be withdrawn, leaving undisturbed any barium carbonate which settles to the bottom. The siphon is filled by applying suction to the tube *D*, which is filled with soda-lime, or pressure may be applied at *B*. The long arm of the siphon may be adjusted so that the end is opposite the zero-mark on the burette, and any excess of alkali drawn over will flow back into the stock-bottle.

385. Alcoholic Caustic-potash Solution is frequently used for the titration of ORGANIC ACIDS with phenolphthalein as the indicator. Such a solution is of twofold advantage. Many of the organic acids are insoluble in water, but dissolve readily in alcohol. Alcoholic solutions of caustic potash are free from carbon dioxide, because potassium carbonate is almost absolutely insoluble in alcohol. On dissolving the caustic potash in the alcohol, the potassium carbonate remains undissolved. After standing twenty-four hours the clear solution may readily be siphoned off from the potassium carbonate, which adheres quite firmly to the bottle. The alcohol used must first be freed from aldehyde or organic material extracted from the oak-barrel, which turns yellow on the addition of alkali and interferes with the titration. For this purpose a stick of caustic potash is added, and after standing for some time the alcohol is distilled off. The caustic-potash solution must be protected from the carbon dioxide of the air by the method suggested for caustic soda or some similar device.

386. Water Solutions of Barium Hydroxide have been largely used when the presence of carbon dioxide would be objectionable. Any carbon dioxide which enters the solution is immediately precipitated as the insoluble barium salt. A solution saturated with barium hydroxide at the ordinary temperature is about two-fifths normal. After shaking the solution with excess of the commercial barium hydroxide until no more dissolves, the clear liquid should be siphoned off and diluted a little before standardizing so as to prevent the crystallizing out of the barium hydroxide during occasional periods of low temperature. This alkali gives a very sharp end-reaction with phenolphthalein.

387. Ammonia.—On account of its volatility strong solutions of ammonia cannot be used. Even with tenth- or fifth-normal solutions the loss of alkali is considerable if the solution is kept in a half-filled bottle and is poured out into the burette. During this process the air above the liquid is largely replaced, and as the pressure of the ammonia vapor is proportional to the concentration of the ammonia in solution, the loss in any case is considerable. The action of the ammonia on the glass is comparatively slight, especially if the same bottle is used continually. The amount of carbon dioxide absorbed is also inconsiderable. If therefore the ammonia solution is siphoned out of the bottle, a fifth- or tenth-normal solution will show only inappreciable changes in strength from day to day, and if kept in an old bottle may be used for considerable periods without change of titre.

EXERCISE 52.

Preparation of N/5 Caustic Soda and Determination of Ammonia in Ammonium Chloride.

Weigh out roughly about 10 grams of pure caustic soda, dissolve in water, and dilute to 1 liter. Place in a bottle provided with a rubber stopper. Standardize by titrating against standard hydrochloric or sulphuric acid, using methyl orange as the indicator. Use at least 25 c.c. of alkali for each titration. If the acid is exactly N/5 normal, divide the number of cubic centimeters of alkali by the number of cubic centimeters of acid used. The quotient multiplied by 1000 gives the number of cubic centimeters of the alkali to be diluted to 1000 to make a N/5 solution. Verify the strength of the diluted solution by titrating against the standard acid.

Weigh out 250 mg. of ammonium chloride and transfer to a 300-c.c. Jena beaker. Dissolve in 50 c.c. of water and add 50 c.c. of the caustic-soda solution. In a similar beaker place 50 c.c. of water and 50 c.c. of the caustic-soda solution. Place both beakers on the hot plate and warm, finally to boiling, until no more ammonia is evolved. Cool both beakers, and titrate the alkali remaining in each with the standard acid, using methyl orange as the indicator. The difference between the amounts of acid used to neutralize the alkali in the beakers is the amount necessary to neutralize the ammonia in the ammonium chloride. 1 c.c. of N/5 acid = .003407 gram of ammonia or .0107 gram of ammonium chloride. Compute the percentage of ammonia as well as of ammonium chloride in the sample analyzed.

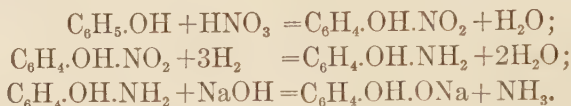
THE KJELDAHL METHOD OF DETERMINING NITROGEN.

In 1883 Kjeldahl described a method for determining nitrogen in organic substances which, with the numerous modifications which have since been suggested, is now the method most largely used for the determination of nitrogen, not only in organic compounds of the greatest diversity of composition, but also in nitrates and other inorganic compounds. There are very few nitrogen compounds in which by one or the other modification the nitrogen cannot be determined with a degree of accuracy and with a rapidity almost unequalled by any other quantitative method.

388. Oxidation of Organic Matter and Conversion of Nitrogen into Ammonium Sulphate.—By the original method the organic material was digested hot with concentrated sulphuric acid, by which the carbon was oxidized to carbon dioxide, while the nitrogen remained as ammonium sulphate. The oxidation was completed by the addition of powdered potassium permanganate. The concentrated acid was then diluted somewhat, and neutralized with caustic soda. The ammonia liberated was distilled off, and determined by means of standard sulphuric acid. In many cases the combustion of the carbon was very slow. Various modifications have been introduced to overcome this difficulty. The addition of *mercury*, *mercuric oxide*, or *copper oxide* or *sulphate* greatly shortens the time of combustion, probably by acting as carriers of oxygen, the metal being alternately oxidized by the sulphuric acid and reduced by the carbon. The addition of *phosphorus pentoxide* or *potassium sulphate* serves the same purpose by raising the temperature to which the solution may be heated. When mercury has been added to the sulphuric acid it must be removed by means of sodium sulphide before the ammonia is distilled off, otherwise some of the ammonia combines with the mercuric oxide and cannot be expelled by distillation.

389. Reduction of Nitrates.—By the original Kjeldahl method the conversion of nitrates to ammonia was very uncertain. To overcome this difficulty, *salicylic acid* or *phenol* was dissolved in the sulphuric acid. This solution first converts the nitrate into nitro-phenol. This compound is readily reduced to amido-phenol,

which is completely hydrolyzed by caustic soda with liberation of ammonia. These reactions take place according to the following equations: *



The reduction is greatly assisted by the addition of sodium thio-sulphate or zinc. The addition of pure cane-sugar is also advantageous when substances of high nitrogen content are oxidized.

390. Kjeldahl Digestion-flasks.—The digestion of the nitrogenous substance with sulphuric acid is carried out in pear-shaped, long-necked flasks of Bohemian or Jena glass which are made for this purpose. The flasks are made of various sizes, since some material foams considerably on being heated with the sulphuric acid, and therefore requires the use of a larger flask. Some workers also desire to obviate the transference of the sulphuric-acid solution from the digestion-flask to a special distillation-flask. If this method is pursued, a digestion-flask capable

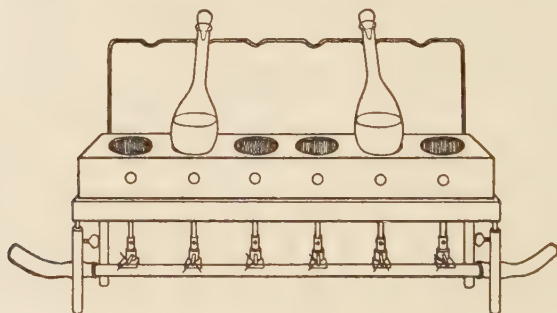


FIG. 47.

of holding about 500 c.c. must be used. If a separate distillation-flask is employed, the digestion-flask need not ordinarily have a capacity of more than 200 c.c.

391. Digestion.—During the digestion the flask is placed so as to be inclined at an angle of 45° , in order that there shall be no loss of material by spattering, nor any contamination by the falling

* These reactions are in reality more complicated than represented, as several sulphuric acid molecules are combined with the benzene radicle. The reactions as given simply show the transformation of the nitric-acid radicle into ammonia.

in of foreign material. As an additional precaution some workers close the mouth of the flask by means of a stopper made by drawing out a glass tube which is somewhat larger than the neck of the digestion-flask. The drawn-out end is sealed, and after cutting off about an inch of the glass tube the stopper is inserted with the drawn-out end in the neck of the flask. Racks for holding six or eight flasks in an inclined position are used where much work must be done. These racks are provided with a Bunsen burner under each flask. If the material froths much, the flask is at first heated with a small flame and over a wire gauze. The heat is gradually increased until finally the flask is heated with the bare flame, until the acid is colorless or a light yellow. The digestion requires from one-half to several hours. As fumes of sulphuric acid and sulphur dioxide are copiously evolved, the digestion must be conducted under a hood.

392. Distillation.—After cooling, the acid is diluted somewhat and transferred to the distillation-flask, if a separate flask is used for this purpose. The distillation-flasks should have a capacity of 500 to 600 c.c. and should be made of hard Bohemian or Jena glass. They may be round-bottomed or of the Erlenmeyer form. To prevent the carrying over of the caustic alkali in the form of spray, a trap of some kind must be interposed between the distillation-flask and the condenser. The simplest form consists of a glass bulb 4 to 5 cm. in diameter filled with glass wool. In another trap shown in Fig. 48, which is very much used, the upper exit tube extends into and is somewhat curved towards the side of the bulb. The rate of distillation is much increased by covering the bulb with thin asbestos paper, which may be made to adhere by simply moistening with water. It is then pressed with the hand around the bulb.



FIG. 48.

The trap is connected to the distillation-flask by means of a rubber stopper and to the condenser-tube by means of a piece of thick-walled rubber tubing. The tube of the condenser must be of *block tin*. Glass cannot be used, as it is dissolved by the steam and ammonia vapor, increasing the alkalinity of the distillate. The condenser-tube is curved downwards, where it is joined to

the trap. A number of these block-tin tubes are frequently passed through the same condenser, which consists of a copper or iron tank of convenient size, as shown in Fig. 49.

The DISTILLATE is received in an Erlenmeyer flask of 300- to 400-c.c. capacity, in which a measured amount of standard sulphuric acid has been placed. If the condenser is supplied with a sufficient amount of cold water, it appears to be unnecessary for the end of the condenser-tube to dip into the standard acid. It is customary, however, to attach a large-sized glass tube to the exit of the tin condenser-tube by means of a piece of rubber tubing.

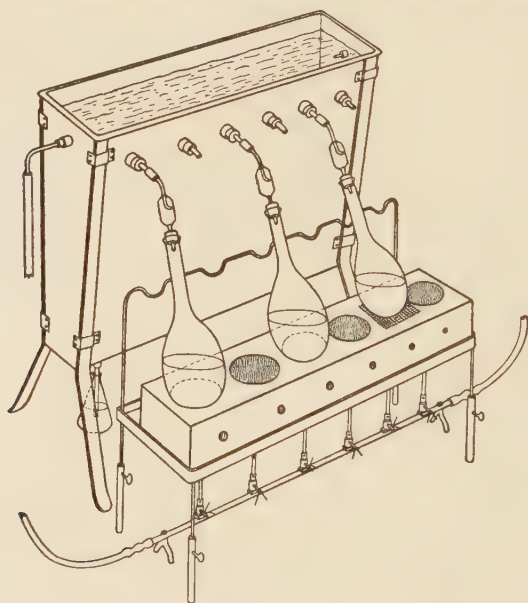


FIG. 49.

The end of this glass tube should touch the surface of the acid. All of the ammonia is usually carried over when 150 c.c. of liquid has distilled over. Until experience is gained it is advisable to continue the distillation after the Erlenmeyer flask containing about 150 c.c. of distillate has been removed. The distillate is then allowed to flow into a small beaker containing a drop of the indicator. If the distillate is still alkaline, the contents of the beaker are poured into the Erlenmeyer flask. The bumping which so frequently accompanies the boiling of an alkaline solu-

tion may generally be prevented by the addition of a few grams of granulated zinc. Bumping is also very much reduced if caustic soda free from carbonate is used. A small piece of paraffine will prevent foaming of the liquid.

393. Titration of Ammonia.—The excess of acid in the distillate is titrated back with standard alkali, which may be caustic soda, potash, or ammonia. The indicator used may be methyl orange, litmus, or cochineal. As the various reagents used may contain more or less nitrogen, a blank must be conducted whenever one or more of the reagents is used for the first time. For the blank determination pure cane-sugar is digested, and care must be taken to add each of the reagents in the amount used in the actual analysis. The amount of nitrogen found in this determination is deducted from each result subsequently obtained with the reagents tested.

WILFARTH'S MODIFICATION

APPLICABLE TO SUBSTANCES FREE FROM NITRATES.

One gram of the finely powdered substance is placed in the digestion-flask, 1 gram of metallic mercury or about 0.7 gram of mercuric oxide is added, and 25 c.c. of a solution of 200 grams of phosphorus pentoxide in 1 liter of concentrated sulphuric acid (sp. gr. 1.84). After digesting and transferring the acid to the distillation-flask with about 200 c.c. of water the mercury is precipitated by the addition of 25 c.c. of a solution of 40 grams of potassium sulphide in 1 liter of water. The acid is then neutralized by the addition of a saturated solution of caustic soda, of which about 50 c.c. will be required. After the addition of a few grams of granulated zinc the ammonia is distilled into the sulphuric acid, of which 50 c.c. of N/5 acid is usually ample. The excess of acid is titrated back with N/5 or N/10 alkali.

GUNNING'S MODIFICATION

APPLICABLE TO SUBSTANCES FREE FROM NITRATES.

Gunning's improvement consisted in the addition of potassium sulphate to the sulphuric acid, by which the time of digestion is considerably reduced. Sodium sulphate may also be used as

well as sodium pyrophosphate. A very excellent digestion mixture consists of 20 c.c. of the mixture of phosphorus pentoxide and sulphuric acid, given in Wilfarth's modification, to which 10 to 15 grams of potassium sulphate are added, either in the beginning or after the first violent oxidation is ended. Excellent results may be obtained with this mixture without the addition of mercury, though the oxidation is considerably hastened by the addition of the usual amount of the latter. The decomposition is frequently complete in thirty minutes and rarely requires more than an hour. The precipitation of the mercury, neutralization, distillation, etc., are carried out as given in the Wilfarth modification.

GUNNING-JODLBAUER MODIFICATION

APPLICABLE TO NITRATES.

In this modification the digestion is carried out with sulphuric acid which contains 40 grams of phenol or salicylic acid per liter. 1 gram of the nitrogenous substance is placed in the digestion-flask and dissolved in 30 c.c. of the phenol-sulphuric acid. The solution should be kept cold and thoroughly shaken to hasten the solution. 2 to 3 grams of zinc-dust and 1 gram of mercury are then added while the flask is shaken and cooled. After standing one to two hours the flask is heated, at first gently, then more strongly. 10 to 15 grams of potassium sulphate may then be added, and the flask heated until the solution is colorless or nearly so. The remainder of the process is conducted as directed for the other modifications.

FÖRSTER'S MODIFICATION

APPLICABLE TO NITRATES.

Having failed to obtain all of the nitrogen from nitrates by the previous modification, Förster introduced the use of sodium thiosulphate as a reducing agent. He treated $\frac{1}{2}$ gram of the nitrate in the digestion-flask with 15 c.c. of a 6% phenol-sulphuric acid, and after the nitrate was completely dissolved 1 to 2 grams of sodium thiosulphate were added. When the decomposition of the thiosulphate is complete 10 c.c. of concentrated sulphuric

acid and 1 gram of mercury are added. The decomposition is completed in the usual manner. The thiosulphate must not be added before the addition of the phenol-sulphuric acid, or nitrogen will be lost. The solution need not be cooled as in the Jodlbauer modification. The oxidation is generally complete in $1\frac{1}{2}$ hours.

394. Substances Decomposed with Difficulty.—In regard to the substances which cannot be determined by the Kjeldahl method and its modifications Dyer* states that the nitrogen in aromatic nitro-compounds cannot be determined by simple reduction with zinc. Phenol or salicylic acid must be present. The same thing is true of many of the azo compounds. Hydroxylamine and acetaldoxime required the addition of sugar before all of the nitrogen was converted into ammonia by the Jodlbauer method. The cyanide and ferrocyanide of potassium could be analyzed by the Gunning modification, while the ferricyanide required the Förster modification. Phenylhydrazine could not be correctly analyzed by any modification. H. C. Sherman† states that where large proportions of chlorides and nitrates exist together all modifications fail.

EXERCISE 53.

Determination of Nitrogen in Milk by the Kjeldahl-Gunning Method.

395. Standard Solutions.—For this determination a fifth normal acid and alkali will be needed. The fifth normal sulphuric- or hydrochloric-acid solution already prepared may be used. The fifth-normal solution of caustic soda may also be used, or a fifth-normal solution of ammonia may be prepared as follows: About 15 c.c. of concentrated ammonia (sp. gr. 0.90) are diluted to 1 liter. A second liter is made in the same manner as the first. The entire solution is well mixed in a large bottle, and then titrated against the N/5 standard acid, using cochineal or methyl orange as the indicator. The solution of ammonia, which is somewhat stronger than fifth-normal, is then diluted to the exact strength, and placed in a bottle connected with the burette by means of a siphon, as described on p. 280. The soda-lime tube may be omitted. A simpler arrangement, which answers fully as well for this purpose, consists of a suitable-sized bottle, closed

* Chem. Centr., III, XVII, 433.

† J. Am. Chem. Soc., XVII, 567.

by a two-holed rubber stopper through which a siphon passes, the long arm of which is outside the bottle. To the end of the long arm is attached, by means of a short piece of rubber tubing, a piece of glass tubing. A pinch-cock is placed on the rubber tube. By opening this pinch-cock and forcing air through the second opening in the stopper, the siphon may be filled. The burette is filled by opening the pinch-cock and allowing the solution to flow out.

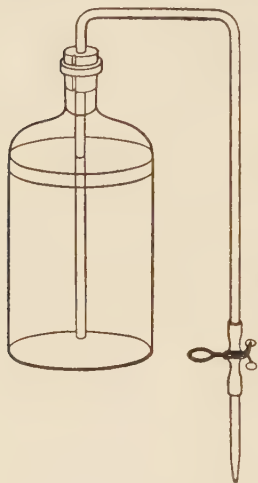


Fig. 50.

396. Weighing the Sample.—The sample of milk to be analyzed must be thoroughly mixed by shaking the bottle. 10 c.c. is withdrawn with a pipette and allowed to flow over the asbestos contained in a *Hofmeister capsule*. The asbestos must be first ignited, and after placing in the capsule, the whole is weighed. After the milk has been added the whole is again weighed. Neither of these weights need be taken closer than several milligrams. A second or even a third sample of milk is weighed out in the same manner. The milk is evaporated to dryness on the water-bath, the capsule crushed in a clean porcelain mortar and transferred to the digestion-flask.

The milk may also be evaporated in the flasks, the weight then being obtained from the specific gravity, or the average weight of 10 c.c. may be obtained by first weighing several portions in small beakers. The evaporation in the flasks is slow unless the steam is displaced by a stream of air. The water may also be boiled out after the addition of the digestion-mixture.

397. Digestion.—Weigh out 20 grams of phosphorous pentoxide in a beaker, and add 500 c.c. of concentrated C. P. sulphuric acid. Stir until solution is complete, and transfer to a glass-stoppered bottle. Transfer 20 c.c. portions of this solution to the digestion-flasks containing the milk, and also to two other flasks in each of which about a gram of granulated sugar has been placed. Add 10 grams of potassium sulphate to each flask, and heat gently over the wire gauze with the Bunsen burner. The heating is conducted under the hood. Increase the heat as the frothing ceases, finally remove the wire gauze, and heat strongly until the solution is colorless or only a light yellow.

While the solution is digesting a saturated solution of caustic soda is made by dissolving 200 grams in twice this amount of water. 40 or 50 c.c. of the standard acid is measured out into each of the Erlenmeyer flasks to be used as receivers. If the condensers of the distilling apparatus have not been recently used, they are cleaned by passing through them the steam from a flask of water strongly acidified with sulphuric acid until

the distillate is no longer alkaline to cochineal solution. If 100 c.c. of the laboratory supply of distilled water reacts alkaline with the cochineal solution, ammonia-free water should be made by condensing the steam from a flask of water acidified with sulphuric acid. This steam should be condensed by passing it through one of the block-tin tubes of the Kjeldahl condenser. This distilled water should then be used for diluting the concentrated acid and whenever needed during the titrations.

398. Distillation.—When the digestion-flasks have cooled, about 50 c.c. of water are added to each, and if the small-sized digestion-flasks have been employed, the solutions are transferred to the distillation-flasks, using about 150 c.c. of the ammonia-free water to rinse out the digestion-flasks. The acid is neutralized with the concentrated caustic-soda solution, of which about 50 c.c. will be required. 2 or 3 grams of granulated zinc are added and the flask is immediately connected with the condenser to prevent loss of ammonia from the hot alkaline solution. The distillation of the ammonia in the first flask is begun immediately, and the acid in the other flasks is diluted, transferred, and neutralized in rotation.

399. Titration.—When about 150 c.c. of distillate has passed into the first Erlenmeyer flask, it is replaced by a small beaker containing a little of the indicator. If 10 or 15 c.c. of the distillate does not react alkaline with the indicator, 2 or 3 drops of the cochineal are added to the solution in the Erlenmeyer flask and the excess of acid titrated with the standard alkaline solution. If the latter has not been compared within a day or two with the standard acid, a measured volume must be titrated against the acid. The other Erlenmeyer flasks should be removed and the solutions titrated in the order in which the acid solutions were transferred to the distillation-flasks. After deducting the average amount of acid neutralized by the ammonia obtained in the blank determinations, the amount of nitrogen found is computed by the factor 1 c.c. of N/5 acid = .002802 gram of nitrogen. To obtain the percentage of casein, the percentage of nitrogen is multiplied by the commonly used factor 6.25 or by the more recently obtained and probably more correct factor 6.43.

EXERCISE 54.

Determination of Nitrogen in Potassium Nitrate by the Förster Modification of the Kjeldahl Method.

For this determination it is advisable to use a sample of pure potassium nitrate as a check on the process. A sample of commercial sodium or potassium nitrate may then be analyzed.

Twenty grams of phenol are dissolved in 340 grams of concentrated sulphuric acid. A solution of potassium sulphide is made by dissolving 20 grams of the commercial article in 500 c.c. of water. $\frac{1}{2}$ -gram portions of the nitrate are weighed out and transferred to digestion-flasks and dis-

solved in 15 c.c. of the phenol-sulphuric-acid solution. After the nitrate is completely dissolved, 1 to 2 grams of sodium thiosulphate are added. When the reaction due to the latter is ended, 10 c.c. of concentrated sulphuric acid is added and about 1 gram of metallic mercury. The mercury may be dropped from a glass tube the end of which is partially closed by fusion or drawing out. The size of this opening may readily be so adjusted that one drop shall weigh about 1 gram. A blank determination is made by treating about 1 gram of sugar with the reagents as already given. The digestion and the subsequent operations are carried out exactly as given in the preceding exercise, except that after the acid solution has been transferred to the distillation-flask, 25 c.c. of the potassium-sulphide solution are added. 1 c.c. of N/5 acid is equal to one five-thousandth of the molecular weight of potassium nitrate or the same proportion of the molecular weight of sodium nitrate.

CHAPTER XXIII.

TITRATION OF BORIC AND CARBONIC ACIDS.

ESTIMATION OF BORIC ACID.

THE titration of boric acid cannot be carried out by means of any indicator in the ordinary manner of titrating an acid, on account of the very weak acid properties of this substance. Because of this peculiarity, the base in many of the salts of boric acid may be readily titrated by means of a strong mineral acid and methyl orange as the indicator without the removal of the boric acid, which is entirely neutral towards methyl orange. Because of the difficulty of carrying out the gravimetric methods which have been devised, the discovery of a method of increasing the acid properties of this acid so that it can be titrated with phenolphthalein as the indicator has been very welcome to chemists.

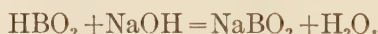
400. Thompson's Glycerine Method.—The method proposed by R. T. Thompson* consists in the addition of enough glycerine to constitute 30% of the solution when the titration is complete. In such a solution the boric acid acts as a monobasic acid. To secure a solution which shall contain no free alkali nor acid except boric acid, the borate is dissolved in water and the solution neutralized with sulphuric acid after the addition of a drop of methyl orange. A drop or two of acid is then added and the solution boiled in an open dish for a few minutes to expel carbon dioxide. A dilute solution may be boiled in this manner for fifteen minutes without the loss of more than a faint trace of boric acid.† Dilute caustic-soda solution is now added until the pink color of the methyl orange just disappears. Glycerine is then added in such amount that after completion of the titration at least 30% shall be

* Jour. Soc. Chem. Ind., XII, 432.

† L. de Koningh, Jour. Am. Chem. Soc., 1897, 385.

present. After the addition of a drop of phenolphthalein the solution is titrated with fifth-normal caustic soda which is free from carbon dioxide. The usual pink end-point of the phenolphthalein is obtained when a slight excess of the alkali has been added. More glycerine should then be added, and if the pink color of the phenolphthalein fades, more alkali must be added. A blank determination should be carried out to determine the acidity of the glycerine. For this purpose the same amount of glycerine should be diluted with an equal volume of water and the solution titrated with the standard alkali.

If ammonia is present, it must first be removed by adding a slight excess of sodium carbonate and evaporating the solution down to half its bulk. By this treatment any iron present will be precipitated and should be filtered off. The neutralization of the boric acid with caustic soda takes place according to the following equation:



1 c.c. of normal caustic alkali is therefore equal to .035 gram of B_2O_3 .

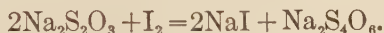
401. Jones's Mannitol Method.—Another method of titrating boric acid has been based on the fact that in the presence of mannitol the acidity is sufficiently increased to allow of its titration with phenolphthalein as the indicator.* The solution may be neutralized in the same manner as given in the glycerine method. Phenolphthalein is then added and standard alkali introduced until the solution is red. A pinch of mannitol is then thrown in, which bleaches the red color. Enough alkali is added to produce a slight alkaline reaction, followed by mannitol until a permanent red color is produced which cannot be discharged by further addition of mannitol. 1 or 2 grams of mannitol is usually sufficient.

The author of this method, instead of using methyl orange as the indicator to secure a solution free from acids except boric, utilizes the fact that a mixture of potassium iodide and iodate is entirely unaffected by free boric acid, while strong mineral acids liberate iodine, thus destroying the free mineral acid according to the following equation:



* L. C. Jones, *Am. J. Sci.*, 1898, pp. 147-153.

The free iodine is removed by adding sodium thiosulphate solution, which combines with the iodine, producing only neutral compounds as follows:



The amount of free mineral acid present may be estimated by determining the amount of free iodine, as will be shown in the next chapter.

The solution of the borate, the volume of which should be about 50 c.c. and which should contain about 0.1 gram of boric acid, is made slightly acid with hydrochloric acid. To precipitate carbonic acid 5 c.c. of a 10% solution of barium chloride is added. A mixture of a solution of potassium iodide and iodate is made in a separate beaker. About 2 grams of the iodide and $\frac{1}{2}$ gram of the iodate are generally sufficient to destroy all the mineral acid present, unless the amount is excessive. Starch solution is added to the iodate solution, and if a blue color develops, it is removed by the cautious addition of dilute sodium thiosulphate solution. A drop of the borate solution added to the iodate should produce a blue color, indicating the presence of free hydrochloric acid, and the certainty of the presence of all boric acid in the free state. The two solutions are then mixed, and the iodine liberated is removed by the addition of sodium thiosulphate. The colorless solution now contains only starch, neutral chlorides, potassium tetrathionate, iodide, and iodate, and the total amount of the boric acid to be determined in the free condition. Phenolphthalein is now added and the boric acid titrated, the mannitol being added as already directed. The end-reaction by this method is sharper than that in Thompson's method.

402. Decomposition of Organic Matter containing Boric Acid.—

Boric acid must frequently be determined in food products, and the separation of the organic matter is first necessary. Thompson proceeds as follows: 100 grams of the sample is made strongly alkaline with lime-water, evaporated to dryness in a platinum dish, and cautiously heated until the organic matter is thoroughly charred so as to give a colorless solution. 20 c.c. of water is added, and the solution acidified with hydrochloric acid, when all but carbon will be in solution. The whole is transferred to a 100-c.c. flask and 0.5 gram calcium chloride added. A few drops of

phenolphthalein are introduced, then caustic soda until a slight pink color is produced, and finally 25 c.c. of lime-water. By this treatment the carbon dioxide as well as other weak acids, such as phosphoric acid, which may be present are precipitated as calcium salts. This solution is made up to 100 c.c., thoroughly shaken, and filtered through a dry paper. To 50 c.c. of the filtrate normal sulphuric acid is added until the pink color disappears, then a drop or two of methyl orange is introduced and acid is again added until the yellow color is just changed to pink. Fifth-normal caustic soda is then added drop by drop until the liquid assumes the yellow tinge, excess of soda being carefully avoided. The solution is boiled until the carbon dioxide is *entirely expelled*. It is then cooled and the boric acid titrated, using phenolphthalein and glycerine or mannitol as the indicator.

DETERMINATION OF CARBONIC ACID IN WATER.

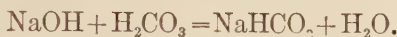
The determination of the percentage of carbonates and bicarbonates when existing as alkali salts, and in the case of the former in the presence of caustic alkali, has already been given. The determination of carbonic acid when present as an insoluble carbonate is best carried out gravimetrically, as given in Chapter IX. Carbon dioxide existing in solution, as in natural or artificial mineral waters, is generally determined volumetrically. It exists in three conditions in such waters: as **FREE CARBONIC ACID**; as **SEMICOMBINED ACID**, or **BICARBONATES** of the alkali or alkaline-earth metals; and as **COMBINED ACID**, or **CARBONATES** of the alkali metals.

403. **The Percentage of Free Carbon Dioxide** may be determined by titrating 100 c.c. of the water with a standard solution of caustic soda or sodium carbonate after the addition of a few drops of phenolphthalein. The alkali should be dilute, tenth or twentieth normal being convenient. When sufficient alkali has been added to give a faint pink to the indicator, all the carbon dioxide has been converted into bicarbonate and a slight excess of carbonate is present, which produces the color with the indicator. The titration must be repeated, adding at once nearly all the alkali used in the first titration, as some carbon dioxide may have been lost during the stirring of the acid solution.

If free carbon dioxide is present, normal carbonates must be absent, since such salts would react with the free acid to form bicarbonates as follows:



Only bicarbonates, therefore, can exist in a solution containing free carbonic acid. On the addition of caustic soda the following reaction takes place:



40.058 parts of caustic soda are therefore equivalent to 44 parts of carbon dioxide. 1 c.c. of N/10 caustic soda will therefore be equal to .004400 gram of CO_2 .

With sodium carbonate solution the following reaction takes place:



106.1 parts of sodium carbonate are therefore equal to 44 parts of carbon dioxide. 1 c.c. of N/10 sodium carbonate solution will therefore be equal to .0022 gram of CO_2 . The use of an alkaline solution of which 1 c.c. is equal to 1 mg. of carbon dioxide is very convenient. 2.412 g. of sodium carbonate are equal to 1 g. of carbon dioxide $\left(\frac{106.1}{44} = 2.412\right)$. Probably the most convenient method of procedure is to dissolve 2.412 g. of pure anhydrous sodium carbonate in 1 liter of distilled water from which the carbon dioxide has been expelled by boiling. 1 c.c. of this solution will be equal to 1 mg. of carbon dioxide.

If the water is neutral to phenolphthalein only bicarbonates can be present. The water may be tested for the presence of **FREE MINERAL ACIDS** by titration with the standard solution of alkali, using methyl orange as the indicator. The difference between the amounts of alkali used in this titration and the one in which phenolphthalein is used as the indicator gives the amount of alkali necessary to neutralize the free carbonic acid. In the presence of free mineral acid semi-combined or combined carbonic acid would be absent.

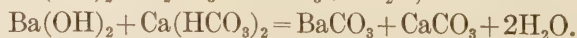
404. The Amount of Semi-combined Carbon Dioxide may be determined by titrating 100 c.c. of the water with dilute standard

acid, using methyl orange as the indicator. The titration with acid and methyl orange gives the amount of semi-combined carbon dioxide only when the water is acid or neutral to phenolphthalein, as normal carbonates are then absent. If the water is alkaline to phenolphthalein free carbon dioxide is absent and only carbonates and bicarbonates can be present. By titrating 100 c.c. of such a water with phenolphthalein and dilute (N/20) acid until the pink color is removed and then adding methyl orange and continuing the addition of the acid until the pink color of the methyl orange is developed, the amount of combined and semi-combined acid may be calculated. The combined carbon dioxide is calculated from the number of cubic centimeters of acid used in the first stage of the titration, 1 c.c. of N/20 acid being equal to .0022 gram of carbon dioxide $\left(\frac{44.00}{20}\right)$, the following reaction taking place:



The number of cubic centimeters of acid used in the second stage of the titration minus the amount used in the first stage gives the amount of semi-combined carbon dioxide, 1 c.c. of N/20 acid being equal, as before, to .0022 gram of carbon dioxide.

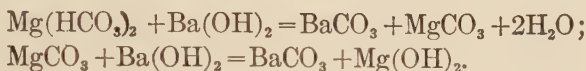
405. The Total Amount of Carbon Dioxide may be obtained by adding together the amount of free carbon dioxide to that semi-combined; or when free carbon dioxide is absent, by adding the amount of semi-combined to the amount combined. The amount of free and semi-combined carbon dioxide is frequently determined by PETTENKOFER'S METHOD. In this process a measured amount of a standard solution of calcium or barium hydroxide is added to a measured volume, generally 100 c.c., of the water to be tested. The free and semi-combined carbon dioxide is precipitated as barium or calcium carbonate with consequent decrease of alkalinity of the solution. The excess of alkali is titrated back with dilute acid. The total amount of carbon dioxide is calculated from the excess of barium hydroxide plus the initial alkalinity of the water:



406. If Sulphates or Carbonates of the Alkalies are present, the precipitated barium salts carry down some of the alkalies unless

the barium was present as chloride, so as to leave the alkali metals as chlorides. For this reason a little neutral barium chloride solution should be added.

407. Determination of Total Amount of Carbon Dioxide in the Presence of Magnesium.—If magnesium bicarbonate is present, an error is introduced into the determination as shown by the following equations:



As the magnesium hydroxide is insoluble the alkalinity of the solution has been decreased by 2 molecules of barium hydroxide, whereas with other bicarbonates but 1 molecule is neutralized. To remedy this difficulty Pettenkofer added 2 c.c. of a saturated solution of ammonium chloride so that the magnesium hydroxide should remain in solution. According to Trillich* this is only a partial remedy of the difficulty. He proposes to omit the addition of the ammonium chloride and apply a correction to the result from a separate determination of magnesium.

The DETERMINATION WAS CARRIED OUT according to Pettenkofer as follows: 100 c.c. of the water are placed in a flask and to it are added 3 c.c. of a 10% solution of calcium or barium chloride and 2 c.c. of a saturated solution of ammonium chloride, as well as 45 c.c. of a solution of barium hydroxide of such a strength that 1 c.c. = 1 mg. of carbon dioxide. The flask is then corked and allowed to stand for twelve hours. 50 c.c. of the clear liquid are withdrawn and the excess of alkali titrated with standard acid. Trillich omits the addition of ammonium chloride, so that the magnesium hydroxide is entirely precipitated. The amount of magnesium hydroxide is calculated from a gravimetric determination, and its equivalent in barium hydroxide subtracted from the amount of barium hydroxide neutralized by the water.

408. Precipitation of Carbon Dioxide as Calcium Carbonate.—When water contains a considerable amount of carbon dioxide so that there is danger of loss during the manipulation, a sample should be collected in a measuring-flask which contains a measured volume of an alkaline solution of calcium chloride made as follows:

* *Zeit. f. angew. Chem.*, 1889, pp. 117, 337.

To one part of crystallized calcium chloride 5 parts of water are added and 10 parts of ammonium hydroxide sp. gr. 0.96. This solution is placed in well-stoppered bottles and allowed to stand several days. The clear supernatant liquid is drawn off as needed. On the addition of this reagent to carbonated water all of the carbonic acid present is precipitated as calcium carbonate. The precipitate is at first amorphous, but on standing for at least twelve hours it becomes crystalline. This change may be hastened by warming on the water-bath. The precipitate must not be filtered off until it has been digested in this manner or stood at least 12 hours. It is then filtered off and washed free from alkali. The carbon dioxide may now be determined in the calcium carbonate by various methods. A very simple method consists in dissolving the carbonate in excess of standard acid and titrating back the excess with standard alkali.

409. If Bottled Carbonated Waters are to be Examined, the bottles may be opened so as not to lose carbon dioxide by a very simple device. An ordinary brass cork-borer of suitable size is taken, and several small holes are drilled a little farther from the cutting end than the length of the cork to be pierced. A rubber tube is securely fastened to the upper end of the borer, and connected to a convenient absorption apparatus containing some of the alkaline calcium chloride solution. The cork of the bottle is pierced with the cork-borer by holding the latter firmly in the hand and turning the bottle around. When one of the small holes in the borer has been brought below the cork the carbon dioxide will pass out through the cork-borer and into the absorption apparatus. When no more carbon dioxide is evolved the bottle is warmed by placing it in lukewarm water, which is then brought nearly to a boil. The absorption apparatus is then disconnected, and the carbon dioxide swept out of the connecting tube by means of air freed from carbon dioxide. The contents of the bottle are added to the liquid in the absorption apparatus, the solution digested on the water-bath for some time, and finally the calcium carbonate is filtered off and washed. The calcium carbonate may then be titrated with standard acid and alkali.

410. Determination of Carbon Dioxide in Gases.—When carbon dioxide occurs in considerable amount in mixtures of gases

it is determined by gasometric methods. When it occurs in amounts considerably less than 1% it is customary to determine it gravimetrically by passing the gas through an appropriate series of absorption-tubes so that the carbon dioxide may finally be weighed. More frequently, however, the carbon dioxide is determined volumetrically.

411. Pettenkofer's Method.—Many methods of procedure and forms of apparatus have been proposed, but nearly all of them follow in general the method suggested by Pettenkofer, which consists in absorbing the carbon dioxide in a measured volume of standard alkali and titrating back the excess. Pettenkofer used barium hydroxide and oxalic acid as the standard solutions. He took a large-sized bottle, aspirated the air to be examined through it until the air already present was completely displaced, and added a measured amount of the standard alkali. On shaking the bottle vigorously for some time the carbon dioxide was completely absorbed. The alkali was poured into a cylinder or bottle, the precipitate allowed to settle, a measured volume withdrawn, and the excess of alkali titrated with the oxalic acid, using phenolphthalein as the indicator.

412. Several Difficulties and Errors are met with in this method. The surface of the glass bottle is capable of holding barium hydroxide so that more alkali is apparently removed from the solution than corresponds to the carbon dioxide present. To overcome this difficulty various remedies have been proposed. The bottle may be rinsed with some of the barium hydroxide solution, washed free from alkali with distilled water, and then dried. A better method much used consists in coating the inside of the bottle with a thin layer of paraffine. This method is successful where a coat of paraffine can be obtained which does not peel off. Still another method consists in shaking the bottle with moist freshly-precipitated barium carbonate. A thin coating of this salt adheres quite firmly to the glass, and acts quite efficiently as a protective agent.

413. Apparatus.—Another source of error is found in the contamination of the barium hydroxide solution with carbon dioxide while being poured from the large bottle into a suitable vessel for allowing the precipitate to settle. In this case the

most serious contaminating influence is the breath of the operator. A form of apparatus recently described by Sewaschen* seems well adapted to overcome this difficulty. The large bottle *A* has a capacity of about 6 liters. The exact volume is carefully determined, most conveniently by the Morse-Blalock bulbs. The volume is taken to a mark *c* on the neck, to which the rubber stopper *B* must always be inserted. The small bottle *C* should have a capacity of very nearly 100 c.c., the exact capacity having been

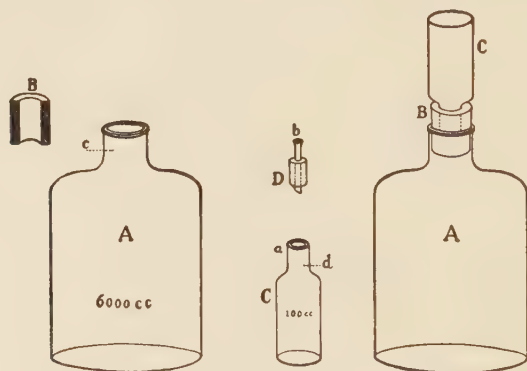


FIG. 51.

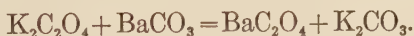
carefully determined when the stopper *D* is inserted to the mark *d* on the neck, the bottle being filled so that no air-bubbles are left under the stopper and the glass rod *b* inserted. The volume of the neck from the point *d* must also be determined and added to that of the large bottle. The neck of the small bottle must be free from any projecting ridge, and must fit quite snugly into the opening in the stopper *B*. If a suitable 100-c.c. bottle is not at hand, a stout 100-c.c. Florence flask may be used. The projecting rim on the neck may be quite readily cut off by means of a diamond, a small flame, or other glass-cutting device.

414. Manipulation.—To use this apparatus, the bottle *A* is cleaned and dried and the inner surface treated by one of the methods already given. The air to be examined is aspirated through the bottle after the stopper *B* is inserted. While the large bottle is being filled with air the standard solution of barium hydroxide is measured out into the small bottle, the stopper *D*

* Hygienische Rundschau, No. 9, 1897.

inserted, and finally the rod *b*. The large bottle is turned on its side and the neck of the small bottle inserted into the stopper *B* after removing the stopper *D*. On turning the large bottle upright the barium hydroxide solution flows out of the small bottle and comes in contact with the air in the large bottle. The latter is shaken occasionally for about two hours, when the absorption of the carbon dioxide will be complete. By inverting the large bottle the barium hydroxide solution will flow into the small bottle, which is then disconnected from the large bottle, the stopper *D* inserted, and the barium carbonate allowed to settle, which requires from twelve to twenty-four hours. Measured volumes are then withdrawn and titrated with the standard acid.

415. Barium Hydroxide has been used most largely as the alkaline solution in which to absorb the carbon dioxide. The barium hydroxide is seldom free from traces of the alkalis, which exert a disturbing influence on the titration when oxalic acid is used and barium carbonate is present. The potassium or sodium oxalate formed in the solution reacts with the barium carbonate as follows:



The potassium carbonate is converted into oxalate by the further addition of oxalic acid. Carbon dioxide is liberated, and the potassium oxalate reacts with more of the barium carbonate, according to the equation given. More oxalic acid is therefore used than corresponds to the amount of free alkali originally present. This action is entirely prevented by the addition of a little barium chloride to the solution, which converts any potassium or sodium salts present into chlorides. The solution must be carefully protected from carbon dioxide by one of the methods already given. It is standardized by titration against standard acid.

416. Oxalic Acid has been most largely used to titrate the excess of the alkali. 2.8636 * grams of the pure recrystallized acid dissolved in one liter of distilled water gives a solution 1 c.c. of which is equal to 1 mg. of carbon dioxide. As dilute solutions of oxalic acid are not stable, a fresh solution must be made as needed by weighing out the crystallized acid.

* Note to student.—Show how this number is calculated.

417. Sulphuric Acid of equivalent strength may also be used with advantage. The presence of barium carbonate does not interfere so much with the titration when sulphuric acid is used. Some workers who use this acid titrate the excess of the barium hydroxide without removing any of the barium carbonate. Alkalies, if present, do not interfere with the titration if sulphuric acid is used. It may be made by diluting a stronger solution. 45.45 c.c. of a normal solution or 227.27 * c.c. of a fifth-normal acid diluted to a liter will give an acid 1 c.c. of which is equal to 1 mg. of carbon dioxide. The acid may also be made by diluting concentrated acid so as to make an approximate solution, which is then standardized by titration with the barium hydroxide solution, which in turn is standardized by titration against weighed amounts of pure crystallized oxalic acid. Phenolphthalein is used as the indicator in all titrations.

418. The Results of the Analysis must be expressed in per cent by volume, the amount of carbon dioxide in the air being given in parts by volume in 10,000. The temperature of the air and the barometric pressure must be taken at the time the large bottle is filled. In very careful work the tension of water vapor in the air must also be taken. The volume of the air at 0° and 760 mm. pressure must then be calculated according to the formula $V_{0^{\circ}.760} = \frac{V(P-p)}{(1+0.0036667t)760}$, where V is the volume of the large bottle used, P is the barometric pressure in millimeters, and t the temperature when the sample of air is taken. p is the tension of water vapor in millimeters of mercury. The amount of carbon dioxide, being obtained in milligrams, must be reduced to cubic centimeters by multiplying the number of milligrams found by .508.

EXERCISE 55.

Determination of Carbon Dioxide in the Air.

419. Standard Solutions.—Prepare a saturated solution of barium hydroxide by treating 15 to 20 grams of barium hydroxide with warm distilled water. Place in a well-stoppered bottle, and when the insoluble matter has settled, draw off by a siphon or large pipette about 250 c.c. and dilute to 1 liter. Protect the solution from the carbon dioxide of the air by placing the solution in a bottle arranged as shown in Fig. 50, p. 290.

* Note to student.—Show how this number is calculated.

Measure out 227.27 c.c. of N/5 sulphuric acid by means of a burette and dilute to 1 liter. If standard sulphuric acid is not at hand, weigh out 2.8647 grams of oxalic acid and dilute to a liter. If the oxalic acid is used, about 0.2 gram of barium chloride must be added to the barium hydroxide solution.

The bottles described on p. 302 are prepared:

420. Collecting the Sample.—The rubber stopper is inserted in the large bottle A, and into the hole of the stopper is inserted a smaller two-holed rubber stopper through which two glass tubes pass, one of which extends to the bottom of the bottle, while the other passes through the stopper only. The tube extending to the bottom of the bottle is connected to a long tube passing out of a window. The smaller glass tube is connected to a Bunsen suction-pump, which is allowed to draw air through the bottle for half an hour. The small bottle is filled with the barium hydroxide solution, the rubber stopper inserted so as not to enclose any air-bubbles, and after pressing it down to the mark, the excess of barium solution is removed and the glass plug inserted.

When the large bottle has been filled with the outside air, the stopper containing the glass tubes is removed. The stopper is also removed from the small bottle, which is inserted into the hole in the stopper of the large bottle, which for this purpose is placed on its side. The temperature is taken from a thermometer which has been hung by the large bottle. The barometer is also read. The large bottle is shaken at intervals for about two hours. It is then inverted, the small bottle containing the barium hydroxide solution is removed, and the stopper inserted.

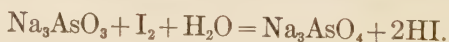
421. Titration.—In the meantime the standard solutions are compared, the titrations being carried out rapidly to prevent absorption of carbonic acid. Phenolphthalein is used as the indicator. If oxalic acid is used, the solution in the small bottle must stand overnight before being titrated. If sulphuric acid is used, it may be titrated when convenient, the glass plug being withdrawn from the stopper, and 25 c.c. of the solution withdrawn by means of a pipette and titrated immediately. Two or three titrations should be made with 25-c.c. portions. The difference between the amount of acid used for these 25-c.c. portions and the amount used in the standardization for 25 c.c. is found and multiplied by the ratio of the volume of the small bottle to 25. This gives the number of cubic centimeters of acid equivalent to the carbon dioxide in the sample of air taken. Calculate the number of cubic centimeters of carbon dioxide by multiplying the number of milligrams by .508. Calculate the volume of air taken at 760 mm. and 0°. Divide the former by the latter and multiply by 10,000 to find the number of parts of carbon dioxide per 10,000.

OXIDATION AND REDUCTION METHODS.

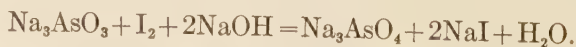
CHAPTER XXIV.

POTASSIUM PERMANGANATE AND DICHROMATE SOLUTIONS.

422. **Oxidation.** — A number of very excellent volumetric methods are based on the fact that many substances exist in two states of oxidation. In the case of arsenic, we have *arsenious* oxide, As_2O_3 , and *arsenic* oxide, As_2O_5 . Sulphur forms several compounds of varying oxygen content, as *sulphurous* acid, H_2SO_3 , and *sulphuric* acid, H_2SO_4 . Substances capable of giving up oxygen, such as POTASSIUM PERMANGANATE, KMnO_4 , convert the former into the latter. The oxidizing substance itself may not contain oxygen, but may be able to oxidize by acting on water or some intermediary substance. IODINE is such a substance which is capable of converting sodium *arsenite* into sodium *arsenate*, as follows:



An alkali must be present to unite with the hydriodic acid so that the action might be represented as follows:



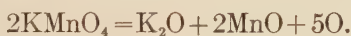
The mechanism of the reaction is probably quite complicated, as many reactions are possible under the circumstances. It may, however, be carried out so that 2 atoms of iodine are equal to 1 atom of oxygen.

The result of the oxidation may not even be the addition of oxygen, as when *ferrous* chloride, FeCl_2 , is converted into *ferric* chloride, FeCl_3 . Perhaps the simplest DEFINITION of OXIDATION is *the change in valence of an element by the addition of negative atoms or radicles or the removal of positive atoms or radicles*. The change in valence may not always be an increase, though it generally is. The oxidation of ammonia may result in a decrease

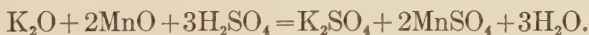
of valence. It is apparent that the reactions taking place during oxidation and reduction are more complicated than those involved in acidimetry and alkalimetry.

423. Normal Oxidizing and Reducing Solutions.—The strength of all oxidizing and reducing solutions may nevertheless be expressed in as simple terms as the acid and alkaline solutions. The *basis selected is oxygen*, the strength of all standard oxidizing solutions being expressed in terms of AVAILABLE OXYGEN or its equivalent in chlorine, iodine, etc. A *normal oxidizing solution is defined as one which contains 8 grams of available oxygen or its equivalent per liter*. HYDROGEN has been selected as the basis of reducing solutions, 1 liter of a *normal reducing solution containing 1 gram of available hydrogen or its equivalent*.

424. Available Oxygen.—The distinction between available and non-available oxygen must be carefully made, just as the acid hydrogens of a molecule must be distinguished from the non-acid atoms in acidimetry. Of the 4 atoms of oxygen in the molecule of POTASSIUM PERMANGANATE but $2\frac{1}{2}$ are available. The decomposition of 2 molecules of this compound may be represented as follows:



The oxidation is generally carried out in acid solution, the potassium oxide and manganous oxide combining with the acid as follows:



Five atoms of oxygen, or 80 parts by weight, being free for oxidation purposes, one-tenth of the gram molecular weight of 2 molecules of potassium permanganate, or 31.63 grams must be dissolved in 1 liter to make a normal solution.

The decomposition of POTASSIUM DICHROMATE is similar:

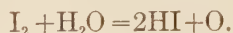


This substance is also used in acid solution, the potassium and chromium oxides reacting with sulphuric acid as follows:



As 3 atoms of oxygen, or 48 grams, are available, one-sixth of the gram molecular weight of potassium dichromate must be dis-

solved in a liter to obtain a solution containing 8 grams of available oxygen per liter. IODINE reacts as follows in the presence of a substance capable of absorbing oxygen:



Two atoms of iodine liberate 1 atom of oxygen. The weight of 1 atom of iodine in grams must therefore be dissolved in a liter to give a normal solution.

425. Indicators.—No indicator is known which directly shows the presence or absence of available oxygen or hydrogen in a solution. POTASSIUM PERMANGANATE serves as its own indicator. As it has an intense reddish-purple color in water solution, and when reduced in acid solution forms the colorless potassium and manganous sulphates, the least excess of the oxidizing solution is indicated by the characteristic permanganate color. As long as even a trace of a reducing substance is present the color fades out by reduction of the permanganate.

As POTASSIUM DICHROMATE is yellow and on being reduced gives the green chromic salts it is impossible to detect the presence of a small amount of the yellow dichromate in the presence of the large amount of green chromic salts. The dichromate solution is generally used with a ferrous iron solution as the reducing substance. In acid solution potassium dichromate instantly converts any ferrous iron present into ferric iron. A very delicate test for ferrous iron is found in the blue color which even very small amounts produce in a solution of POTASSIUM FERRICYANIDE. A solution of ferrous iron to which dichromate solution has been added may be tested for the presence of the former by taking out a drop of the solution and adding it to a drop of the indicator. When, after the successive addition of small amounts of dichromate solution, a test for ferrous iron is no longer obtained, the titration of the ferrous iron is complete.

Solutions of IODINE are deep red to yellow according to the concentration. After reduction the iodine forms colorless salts. If the substance oxidized also forms colorless salts the titration may be conducted by using the IODINE COLOR as the indicator. This gives fairly accurate results, but a much more delicate indicator for iodometric work is found in STARCH SOLUTION, which

gives an intense blue color when the least excess of free iodine is present. Because of the delicacy of this method of obtaining the end-point, iodometric titrations are among the most accurate known to the chemist.

POTASSIUM PERMANGANATE.

426. Decomposition of the Permanganate by Manganese Dioxide.—This salt may now be purchased in a high state of purity. As it is not hygroscopic, solutions made by weighing out the C.P. article and dissolving in water are accurate within less than $\frac{1}{2}\%$. Sulphates, nitrates, and chlorides are the common impurities which must be absent from the C.P. article. It is almost impossible, however, to prepare a sample of this salt which is free from small amounts of manganese dioxide. The injurious effect of this impurity on solutions of potassium permanganate has been clearly shown by Morse and his pupils.* He has proved that the permanganate is slowly decomposed by even traces of the dioxide with liberation of oxygen and formation of more of the dioxide. As the rate of decomposition is proportional to the amount of the dioxide, the decomposition is accelerated with the age of the solution. The remedy consists in the complete removal of the dioxide. This is easily accomplished by *filtering the permanganate solution through asbestos* which has been digested with strong aqua regia and well washed. Organic matter, dust, etc., which may reduce the permanganate with formation of the dioxide must be rigorously excluded from the solution after filtration. All bottles and glassware with which the solution may come in contact must be freed from organic matter by washing with dichromate cleaning mixture. As distilled water usually contains ammonia and organic matter, it is well to allow the permanganate solution to stand some time before filtration so as to entirely decompose this organic matter. The distilled water may also be purified by adding a very little potassium permanganate, boiling until the permanganate is decomposed, and then filtering off the manganese dioxide through asbestos. If the permanganate solution is made up in this manner and kept out of strong sunlight it is very

* Am. Chem. Jour., 18, 411; 23, 313.

permanent, readily keeping its strength for months. Portions of the solution withdrawn from the bottle should not be returned to it.

STANDARDIZATION OF POTASSIUM PERMANGANATE SOLUTIONS.

427. By Pure Iron Wire.—As has been said, permanganate solutions made by weighing out the pure salt are within at least $\frac{1}{2}\%$ of the calculated strength. A higher degree of accuracy is obtained by carefully standardizing the solution. The most largely used and perhaps the most reliable method consists in the use of known amounts of iron. Soft-iron wire containing from 99.6 to 99.8% of iron may readily be obtained. The exact percentage of iron may be obtained by a gravimetric determination of the iron as given in Exercise 11, or of the total carbon, as given on page 374, the iron being found by difference. Formerly the practice was common of dissolving the iron in dilute sulphuric acid, the air having been excluded by means of carbon dioxide. Under these circumstances the iron is converted into ferrous sulphate, which was then titrated with the permanganate. As one of the impurities in the iron is carbon which is combined to a greater or less extent as a carbide of iron, the solution of the wire in acid leads to the formation of hydrocarbons, which are oxidized by the permanganate. As one part of carbon may reduce ten and one-half parts of potassium permanganate, and if the carbon is present as a hydrocarbon it may reduce twice this amount of the permanganate, the error from this source, even if the amount of carbon present is very small, may be very considerable. Titrations of solutions of iron wire have been made which indicate as much as 104% of metal in the wire if calculated on the assumption that the only reducing substance present is ferrous iron. Blair recommends the oxidation of the hydrocarbons by means of potassium chlorate* or potassium permanganate.† If this method is pursued the iron need not be dissolved in an atmosphere free from oxygen, as it must be reduced after oxidation of the organic material. If the chlorate is used the iron is dissolved in hydrochloric acid, a few crystals of potassium chlorate added, and the excess of

* Blair, *The Chemical Analysis of Iron*, 4th Ed., p. 220.

† *Ibid.*, p. 95.

chlorine expelled by boiling. If permanganate is used the iron may be dissolved in sulphuric acid.

428. By Standard Iron Solution.—A very excellent reagent for standardizing permanganate solutions is recommended by Blair.* 100 grams of pure wrought iron free from manganese and arsenic, and in which the phosphorus has been determined, is weighed out and dissolved in nitric acid. The solution is evaporated to dryness and the residue heated in a platinum crucible or dish as hot as possible with the blast-lamp. The ignited material is ground in an agate mortar, dissolved in hydrochloric acid, evaporated to dryness to dehydrate the silica, taken up with hydrochloric acid, and the silica filtered off. The filtrate is diluted to about 4 liters. Portions of this solution of 15 to 25 c.c. are weighed in small flasks and the iron precipitated and weighed as ferric oxide. The weight of the phosphoric acid must be subtracted from the weight of the oxide. The percentage of phosphorus in the iron multiplied by 1.6† will give the percentage by which the weight of the ferric oxide should be reduced. After determining in this manner the exact amount of iron in a weighed portion of the solution, the permanganate may be standardized by taking weighed portions of the ferric chloride solution, reducing the iron, and titrating.

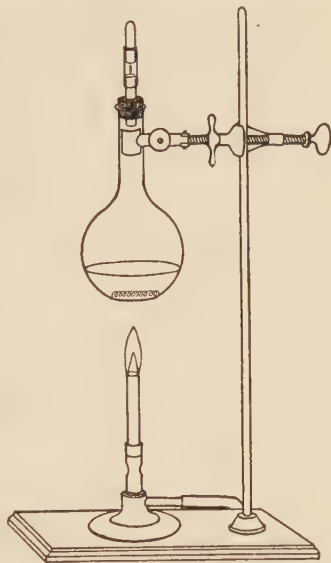


FIG. 52.

429. Reduction of Iron Solutions.—Various methods of reducing the solutions of iron are in use. The most common substance used is GRANULATED MOSSY ZINC. The solution of the iron is placed in a flask of about 250 c.c. capacity. It may be closed with a Bunsen valve, made by cutting a slit a quarter of an inch long with a sharp knife in a small rubber tube which is then closed at one end with a glass plug, while the other end is passed over a short piece of glass tubing which passes through the rubber stopper

* Blair, *The Chemical Analysis of Iron*, 4th Ed., p. 218.

† Note to student.—How is this number obtained?

into the flask, as shown in Fig. 52. The gases within the flask can readily pass out through this valve, while the air cannot enter. The air in the flask is expelled by adding a little sodium carbonate. A few grams of zinc are then added, and the solution warmed nearly to boiling. The sides of the flask must not be heated with the flame of the burner above the point filled by the solution. If hydrochloric acid is present, the complete reduction of the iron is indicated by the change in color from the yellow of the ferric chloride to the light green of ferrous chloride. Sulphuric acid is then added and the solution heated until all of the zinc is dissolved. Cold, recently boiled water is then added and the solution allowed to cool. When the stopper is removed from the flask it should be replaced as soon as possible, a little sodium carbonate having been added to expel the air.

430. Exclusion of the Air.—Another very convenient method of excluding the air consists of inserting into the flask a one-holed rubber stopper through which passes a glass tube bent to a slightly acute angle, so that when the flask is inclined the long end of the glass tube may be vertical, as shown in Fig. 53. This end dips into a saturated solution of sodium bicarbonate. On heating the flask the air is expelled, and on cooling a partial vacuum is formed so that the bicarbonate solution is drawn up into the flask. On meeting the acid solution, carbon dioxide is evolved, which prevents the remainder of the solution from entering the flask. After the addition of zinc and reduction of the iron, sulphuric acid

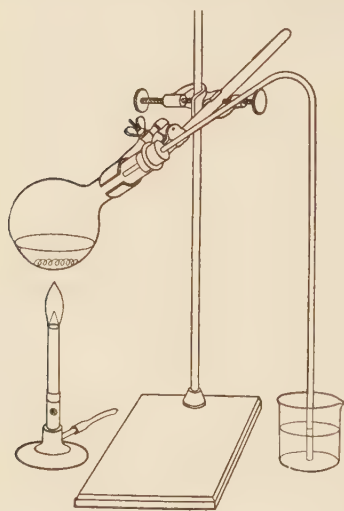


FIG. 53.

is introduced to dissolve the remainder of the zinc. The carbonate solution is removed, boiled and cooled distilled water is added, and the iron solution titrated.

431. Titration of Iron in Zinc.—As it is difficult to obtain zinc which is entirely free from iron, the amount of zinc used must be roughly weighed. The same amount of zinc is weighed out and

treated with sulphuric acid in a flask exactly as in reducing the iron. After all of the zinc has been dissolved the solution is titrated with the permanganate. The amount of solution used in this blank determination is subtracted from the volume of permanganate used in titrating the iron.

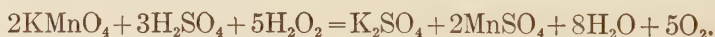
The REDUCTION of the iron solution by means of STANNOUS CHLORIDE, AMMONIUM SULPHITE, and HYDROGEN SULPHIDE are more especially adapted to the reduction of iron in iron ores, and will be described under that heading on page 318. These methods are equally well adapted to the reduction of iron solutions for the purpose of standardization.

432. Ferrous Ammonium Sulphate may also be used for standardizing permanganate solutions. This salt is remarkably permanent. When dry it may be kept for a long time without any appreciable oxidation of the iron. It also retains its water of crystallization with considerable persistence. If a sample of this salt is at hand which is free from ferric iron and has been compared with a standard of known purity, it offers a very convenient method of standardizing permanganate solutions, as the salt may be weighed out, dissolved in water, and, after the addition of dilute sulphuric acid, may be titrated with the permanganate immediately. The iron begins to oxidize very soon after being dissolved, so that the solution must be titrated immediately. As this salt may be titrated just as readily with bichromate solutions, its purity may be tested by titrating a weighed portion with a standard solution of potassium dichromate.

433. Oxalic Acid and the Oxalates, such as potassium tetroxalate prepared and tested exactly as given in Chapter XXI for standardizing alkalis and acids, may be used for standardizing permanganate solutions. It is evident that this class of substances affords a means of comparing standard acids with standard oxidizing solutions. Testing the purity of the oxalic acid by titrating it with a standard acid is of value only when the absence of alkalis from the oxalic acid is assured. This is readily accomplished by igniting a portion of the acid. It should volatilize completely. The titration of oxalic acid with permanganate solution is generally carried out in a warm solution acidified with sulphuric acid. In the cold the oxidation of the oxalic acid is very slow. It may also be accelerated by the addition of man-

ganous sulphate solution. If the solution is warmed, the temperature must not be allowed to exceed 60°, as at a higher temperature small amounts of oxalic acid may be volatilized. At this temperature the beaker can be taken in the hand without serious discomfort. The permanganate solution must be added slowly and with vigorous stirring to the oxalic acid solution. Much manganese dioxide must not be allowed to form in the solution or an excess of permanganate will be required, as the manganese dioxide decomposes some of the permanganate with evolution of gaseous oxygen.

434. Direct Measurement of Oxygen.—An excellent method of standardization which does not require the preparation of a pure substance has been given by G. Lunge.* In this method a measured volume of the permanganate solution is decomposed by means of hydrogen peroxide and sulphuric acid according to the following reaction:



Twice the amount of available oxygen present in the permanganate is evolved in the gaseous form. This gas is measured and the weight of KMnO_4 calculated. LUNGE'S NITROMETER is used for carrying out the determination. The accuracy of the determination depends largely on the accuracy with which the nitrometer has been graduated or calibrated. As the solutions used are already saturated with air the evolution of the oxygen is very quickly complete. The gas is measured in the nitrometer over mercury. The details of the process and a diagram of the nitrometer are given in Exercise 56, page 315.

435. Standard Sulphuric Acid may be used for standardizing a permanganate solution. A measured amount of the standard acid is placed in a beaker and a sufficient amount of hydrogen peroxide to reduce about 25 c.c. of the permanganate solution is added. The peroxide is titrated with the permanganate solution. The faint red color giving the end-point is removed with a drop of the peroxide. Methyl orange is added and the excess of sulphuric acid titrated with standard alkali.

The difference between the amount of acid originally added and that found by titration gives the amount of acid required for the reaction given in the preceding paragraph. It is evident from

* Chem. Ind., 1885, 168; Ber., 18, 1072; Zeit. angew. Ch., 1890, 10.

this equation that 25 c.c. of N/5 potassium permanganate will require 15 c.c. of N/5 sulphuric acid. From this relation the strength of the potassium permanganate solution can be calculated.

The methods of standardization in which a known amount of iron is used are preferred for obvious reasons when the permanganate solution is to be employed for the determination of iron.

EXERCISE 56.

Preparation and Standardization of N/5 Potassium Permanganate Solution.

436. **Preparation and Preservation of the Solution.**—Weigh out 6.35 grams of KMnO_4 . Warm about half a liter of distilled water to about 50° . Add the permanganate with stirring to the warm water. Prepare two carbon filters, using asbestos which has been digested with warm concentrated aqua regia for about an hour and then well washed with water and finally transferred to a stoppered bottle with distilled water. These filters, as well as all vessels with which the permanganate solution is to come in contact, should be freed from organic matter by digestion with cleaning mixture, made by dissolving a few crystals of potassium dichromate in concentrated sulphuric acid. Suck the asbestos down with the filter-pump, being careful to leave a film projecting upwards around the edge. By means of rubber stoppers arrange the filters as shown in Fig. 54. Filter the permanganate solution, being careful not to apply too strong suction for fear of breaking the liter flask. Rinse the beaker carefully and wash the asbestos until the water comes through colorless. After being washed, the asbestos in the second filter should be very nearly pure white. If much brown manganese dioxide is seen, the solution must be filtered again, the filters being interchanged, and clean asbestos put in what is now the second filter. After cooling, the solution is diluted to the mark with distilled water. This solution should be kept in the dark and out of contact with organic matter. Portions taken out of the bottle should not be returned to it.

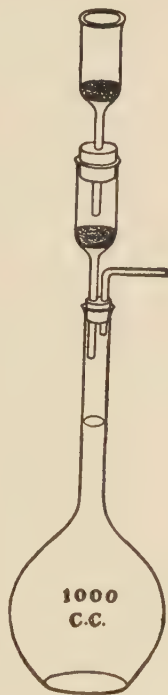


Fig. 54.

STANDARDIZATION.

437. **First Method. By Means of Pure Iron Wire.**—Clean thoroughly by rubbing with sandpaper and filter-paper some soft iron wire in which the percentage of iron has been determined. When cleaned, wind in a spiral on a lead-pencil with as little contact with the fingers as possible. Weigh carefully about 0.250 gram, place it in a 250-c.c. Florence flask, and dissolve

with gentle heat in 10 c.c. concentrated hydrochloric acid and 20 c.c. of water. When the iron is dissolved, throw in a few crystals of potassium chlorate and boil gently a few minutes with a small Bunsen-burner flame. Carefully avoid heating with the flame the sides of the flask above the liquid. Add about 2 grams of granulated zinc which is free from iron. Close the mouth of the flask with a rubber stopper through which passes a bent glass tube dipping into a solution of sodium bicarbonate, as shown in Fig. 53. Heat nearly to boiling till the solution is of a pure green color, free from the slightest tinge of yellow. If the zinc is all dissolved before this point is reached, add another gram and continue heating until all of the iron is reduced. Allow the flask to cool somewhat. The bicarbonate solution will rise in the glass tube and enter the flask only to be expelled by the carbon dioxide evolved when it reaches the acid solution. Add a mixture of 10 c.c. of concentrated sulphuric acid and 20 c.c. of water and again heat until no particles of undissolved zinc remain in the solution or on the sides of the flask. Allow the solution to cool and then add cold but recently boiled distilled water until the flask is about two-thirds full. Titrate immediately with the permanganate solution until a rose-tint is produced which is permanent for two minutes. Repeat the determination until duplicates are obtained agreeing within less than 0.1 c.c.

438. Second Method. By Means of Mohr's Salt.—Weigh out 19.62 grams of pure recrystallized ferrous ammonium sulphate ($\text{FeSO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$). Transfer to a beaker, dissolve in about 100 c.c. of water, and transfer to a 250-c.c. flask. Add 40 c.c. dilute sulphuric acid, shake, cool, and dilute to the mark. This solution will be exactly N/5 normal. Titrate immediately 25-c.c. portions with the permanganate solution until duplicates are obtained and calculate the strength of the permanganate solution in terms of normal.

439. Third Method. By Means of Potassium Tetroxalate.—Weigh out between 0.3 and 0.35 gram of recrystallized potassium tetroxalate and transfer to a beaker. Add about 50 c.c. of water and a few cubic centimeters of dilute sulphuric acid and dissolve by gently heating the solution to 50° or 60° . Be very careful not to heat any higher. Add the permanganate solution slowly with constant stirring. If the solution does not clear readily, warm gently again. When nearly all of the oxalic acid has been oxidized, the solution will decolorize the permanganate almost instantly. At this point add the permanganate cautiously until a faint permanent pink is obtained. If a permanent brown coloration or precipitate is obtained, too much permanganate has been added. Repeat until duplicates have been obtained. One part of the oxalate equals 0.4978 part KMnO_4 .

440. Fourth Method. Determination of Oxygen Evolved with Hydrogen Peroxide.—Set up the Lunge nitrometer as shown in Fig. 55. The box is designed to prevent loss of mercury if any is accidentally spilled. Suspend a thermometer near the nitrometer. Fill with mercury and

test the joints for leaks by lowering the level-tube *A* so as to produce a vacuum in *B* and noticing if the height of the mercury column in *B* remains constant for ten minutes. Now raise the level-tube and produce pressure in the apparatus, and again wait ten minutes to see if the mercury column moves. Measure out into a beaker 15 c.c. of the permanganate solution, and, after acidifying with 10 c.c. of dilute sulphuric acid, add from a burette hydrogen peroxide quite rapidly with stirring until the

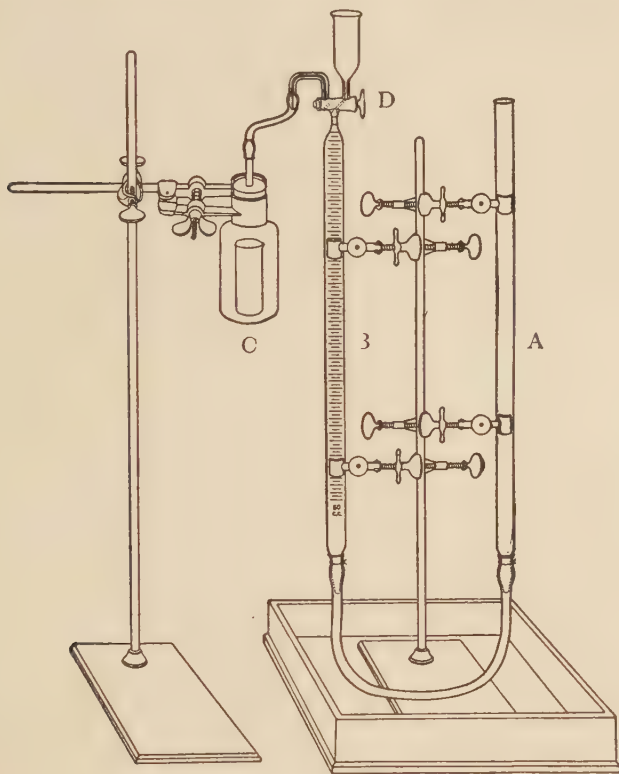


FIG. 55.

solution is clear. Repeat the determination, measuring out the hydrogen peroxide solution first.

Measure out into the bottle *C* the amount of hydrogen peroxide solution found to be equivalent to 15 c.c. of the permanganate solution, adding a slight excess. Add about 10 c.c. dilute sulphuric acid. Measure into the inner tube 15 c.c. of the permanganate solution. Insert the stopper firmly and bring the mercury in the two tubes to the same level. Turn the stopcock of the nitrometer through 180° and bring the mercury in *B* just up to the key of the stopcock, thus expelling the air through the funnel-tube.

After clamping the level-tube, reverse the key of the stop-cock and observe if the mercury falls or rises on connecting the tube *B* with the bottle. If it falls a little, air should be drawn out of *C* by lowering the level-tube. The stop-cock is then reversed, and the air expelled as before. This operation must be repeated until the mercury column in *B* neither falls nor rises when the key of the stop-cock is reversed. If the mercury in *B* rises, air must of course be admitted through the funnel-tube.

The barometer and the thermometer suspended near the gas burette should now be read. The apparatus should then be allowed to stand undisturbed for five minutes to see if the air in the bottle is at the room temperature. Any change in temperature will be indicated by movement of the mercury in *B* up or down, in which case the amount of air in *C* must be again adjusted. The bottle is now tilted slightly and gently shaken, so that the two liquids come in contact. The level-tube is lowered so that no considerable pressure is developed in *B*. The shaking is continued until all of the permanganate is decomposed. The mercury columns are brought to the same level and the apparatus allowed to stand for five minutes. If a change in the volume of the gas has taken place, the bottle is again shaken and the test repeated. When no more gas is evolved, the final adjustment of pressure is made. The mercury surfaces are brought as nearly on a level as possible with the eye. A drop of water is introduced into the funnel-tube and the stop-cock slowly turned. If the pressure within the tube *B* is not identical with the atmospheric pressure, the drop of water will start to move, the direction indicating in which tube the pressure is greater. By raising or lowering the level-tube slightly, the inequality can generally be overcome in a few minutes.

When atmospheric pressure has been secured within the tube *B*, the volume of the gas is carefully read, and after five minutes read again. If no change has occurred, the thermometer and barometer are again read. As the entire determination need not consume more than one hour, neither the temperature nor the pressure usually change an appreciable amount. Compute the volume, at 0° and 760 mm. pressure, of the oxygen evolved. In this computation, the pressure of water vapor must be taken into account by deducting from the observed barometric pressure the vapor tension of water at the observed temperature. 1 c.c. of dry oxygen at 0° and 760 mm. pressure weighs .0014298 gram. 1 gram of oxygen equals 1.977 grams KMnO_4 . Repeat the determination until duplicates are obtained.

DETERMINATION OF IRON IN IRON ORES.

441. Dissolving the Ore.—By digesting the powdered ore on the hot-plate with a mixture of equal parts of water and concentrated hydrochloric acid the iron in some ores is completely dissolved; but most iron ores contain a small amount of *ferrous*

silicate or *titanate* which is not decomposed by hydrochloric acid. After digesting the ore until the residue is white or unaffected by further digestion with hydrochloric acid, it is filtered off and washed free from iron. After burning the paper the silica is volatilized by treatment with hydrofluoric and sulphuric acids. The iron remains in the crucible and may be dissolved by digestion with hydrochloric acid, or it may be fused with acid potassium sulphate. The insoluble material may also be decomposed by fusion with sodium carbonate. If the ore contains organic material a little potassium chlorate must be added to the hydrochloric acid.

442. Reduction of the Iron by Zinc.—The solution of the ore may be deoxidized by means of zinc as given for the standardization of the permanganate solution. This method introduces an error in the determination if *titanium* is present, as it is partially reduced by the zinc. The reduction by ammonium bisulphite or hydrogen sulphide does not affect the titanium. It is carried out as directed in Exercise 57.

443. The Reduction of Iron by Means of Stannous Chloride is very rapid and with the addition of phosphoric acid to the solution to remove the color of the ferric chloride the titration is very exact. The hydrochloric acid solution of the iron is heated nearly to boiling and stannous chloride solution added cautiously until the yellow color of the ferric chloride is replaced by the light green of ferrous chloride. A slight excess of stannous chloride is added and then all at once with vigorous shaking of the flask 60 c.c. of mercuric chloride are added. 60 c.c. of an acid manganous sulphate solution containing phosphoric acid is added and after diluting the solution with cold water it is titrated immediately with the permanganate solution. The manganous sulphate is introduced to prevent reduction of the permanganate by the hydrochloric acid.

The stannous chloride solution is made by dissolving 30 grams of tin in 200 to 300 c.c. of strong hydrochloric acid and diluting to 1 liter after filtering through asbestos.

The mercuric chloride solution is made by dissolving 50 grams of mercuric chloride in 1 liter of water.

One liter of the manganous sulphate solution should contain $66\frac{2}{3}$

grams of crystallized manganous sulphate, $333\frac{1}{3}$ c.c. of phosphoric acid (sp. gr. 1.3), and 133 c.c. of concentrated sulphuric acid.

444. Reduction of Iron by Hydrogen Sulphide.—The iron may also be reduced with hydrogen sulphide. For this purpose the solution is placed in a flask closed with a two-holed rubber stopper, through which passes a glass tube extending nearly to the bottom of the flask. The solution is heated nearly to boiling and hydrogen sulphide passed through the long glass tube until the iron is completely reduced. The stream of hydrogen sulphide is replaced by a stream of carbon dioxide and the hydrogen sulphide expelled by boiling the solution for a few minutes. The flask is cooled while the stream of carbon dioxide is passing and the iron titrated immediately with the permanganate solution. The sulphur is not oxidized by permanganate in the cold.*

EXERCISE 57.

Determination of Ferrous and Total Iron in an Iron Ore.

445. Solution of the Ore.—Weigh out 0.5 gram of the finely powdered ore, transfer to a 100-c.c. beaker, and add 10 c.c. of concentrated hydrochloric acid and 10 c.c. of water. Cover the beaker with a watch-crystal and digest on the hot-plate until the residue is colorless or unaffected by further digestion with the acid. The solution must not be allowed to go to dryness. If necessary add a little dilute hydrochloric acid as the solution evaporates.

Decant the solution into a 250-c.c. flask, transfer the insoluble material to a small filter-paper, and wash with small portions of hot water. Throw the moist paper into a platinum crucible and burn the paper. Add 20 to 30 drops of concentrated sulphuric acid and as much hydrofluoric acid and warm gently. If the material dissolves, continue heating the crucible until the hydrofluoric acid is entirely expelled. If solution is not complete add, after expulsion of the hydrofluoric acid, about $\frac{1}{2}$ gram of acid potassium sulphate and heat the covered crucible sufficiently to fuse the sulphate. When the material is entirely dissolved, let the crucible cool and dissolve the contents in hot water, if necessary adding a little hydrochloric acid.

446. Reduction of the Iron by Means of Sulphurous Acid.—In the meantime the main portion of the ore is reduced by means of ammonium bisulphite. Ammonia is added until a small permanent precipitate of ferric hydrate is produced. 5 c.c. of a solution of ammonium bisulphite, made by

* Jour. Am. Chem. Soc., Vol. XVII, p. 78, 1895; Chem. News, Vol. LXXIII, p. 123, 1896.

saturating strong ammonia with sulphur dioxide, is added and, after shaking vigorously, the solution is gently heated until it is colorless. The solution of the material insoluble in hydrochloric acid is now added, as well as a mixture of 10 c.c. of concentrated sulphuric acid and 20 c.c. of water. The solution is then boiled until the steam no longer smells of sulphur dioxide. The flask is filled with boiled distilled water without mixing with the solution of iron. The flask may be covered with a small watch-crystal and cooled by placing it in cold water. The solution may then be poured into a large beaker or porcelain dish and titrated with the standard permanganate solution. Calculate the percentage of metallic iron present in the ore.

DETERMINATION OF FERROUS IRON.

447. Solution of the Ore.—Weigh out $\frac{1}{2}$ gram of the ore and transfer to the flask *A*, which should have a capacity of about 250 c.c. The simplest method of weighing the ore is to use a glass tube about 10 cm. long, having a diameter of about $\frac{1}{2}$ cm. and sealed at one end. Weigh the tube roughly, introduce about $\frac{1}{2}$ gram of the ore and weigh carefully. Insert the tube in the neck of the flask, and by gently tapping the tube, deposit the ore on the bottom of the flask. Withdraw the tube and weigh again. The difference between the last two weights is the weight of the ore in the flask.

Insert the stopper with the tubes, as shown in Fig. 56. Place a solution of sodium bicarbonate in the beaker and pass a stream of carbon dioxide from a Kipp generator through the tube *B* for about ten minutes. Disconnect the tube *B* at the joint *C* and attach a funnel. Pour in 30 c.c. of dilute hydrochloric acid, raising the tube *D* out of the bicarbonate solution.

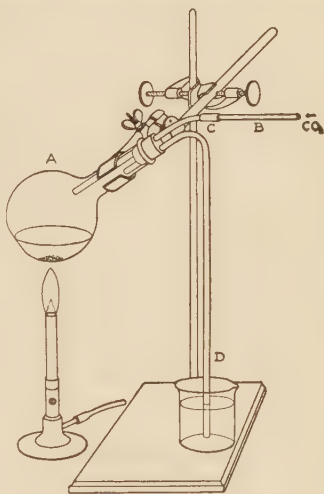


FIG. 56.

Remove the funnel and again connect the tube *B* at *C* and continue passing the current of carbon dioxide. Dissolve the ore in the acid by means of gentle heat from the Bunsen burner.

448. Titration.—When no black particles remain in the insoluble portion remove the burner, replace the beaker of bicarbonate solution with a beaker of boiled and cooled distilled water, disconnect the tube *B* and close *C* with a clamp. Dissolve 3 grams of zinc in 10 c.c. of concentrated sulphuric acid and 20 c.c. of water. When the solution of the iron is cold, add the acid solution of zinc and titrate at once.

449. Calculation.—Compute the percentage of iron present as ferrous oxide. 1 c.c. N/5 potassium permanganate is equal to .01438 gram of ferrous oxide. Compute the percentage of ferric oxide present. For this purpose subtract the number of cubic centimeters of permanganate solution reduced by the ferrous iron in $\frac{1}{2}$ gram of the ore from the number of cubic centimeters required to titrate the total amount of iron present. The difference gives the number of cubic centimeters of permanganate solution required to titrate the iron present as ferric oxide in $\frac{1}{2}$ gram of ore. 1 c.c. of N/5 permanganate solution is equal to .01598 gram of ferric oxide.

ANALYSIS OF MANGANESE ORES.

The only ores of manganese which are of commercial importance are PYROLUSITE and several related ores which consist essentially of manganese dioxide combined with small amounts of the lower oxides of manganese together with more or less iron, silica, and other impurities. Formerly the manganese ore was of value chiefly on account of the oxygen present by which free chlorine, bleaching powder, etc., could be produced. Recently an extended use for manganese has been found in connection with the production of iron and steel, so that nine-tenths of all manganese ores are said to be used for this purpose. The valuation of the manganese ore may therefore require the determination of the available oxygen or the percentage of manganese present.

450. Determination of Available Oxygen.—As the oxygen present is used to evolve chlorine, the most rational method of determination would seem to be to treat the ore with hydrochloric acid and determine the amount of chlorine evolved. This may be done with great accuracy, and the process will be described in the chapter on iodometric methods. This method is not so largely used at present as those in which the ore is dissolved in acid in the presence of a known amount of a reducing agent, and the excess of the latter determined by means of a standard solution of an oxidizing agent. Oxalic acid and ferrous iron have been most largely used as reducing agents with potassium permanganate and potassium dichromate respectively as the standard oxidizing solutions.

The finely powdered material is dried by spreading it out on a watch-crystal and heating for from four to six hours on a water-

bath, or in an air-bath maintained at 100°. The dried material must be weighed quickly, as it is hygroscopic. If oxalic acid is used the ore may be dissolved in an open beaker, as this reducing agent is not affected by the oxygen of the air. If ferrous iron is used the air must be excluded by one of the methods used during the reduction of iron with zinc. It is advisable, both when using oxalic acid and ferrous iron, which is most conveniently introduced as ferrous sulphate or ferrous ammonium sulphate, to weigh out the dry salts instead of making a standard solution of these reducing agents. The reducing solutions, especially of the iron, would require standardization every day, while one titration of the dry salt if preserved in a well-stoppered bottle would be sufficient. The errors of measuring out portions of a solution are also considerably greater than the errors of weighing a salt.

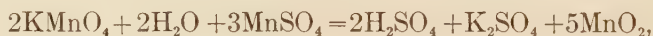
DETERMINATION OF MANGANESE BY VOLHARD'S METHOD.

Manganese may be determined very quickly and accurately by the method of Volhard. The manganese must be in neutral solution as a manganous salt. On adding potassium permanganate to such a solution all of the manganese present, including that which was added as permanganate, will be precipitated as the dioxide. The precipitate has a fairly strong acid character, so that varying amounts of the bases present in the solution will be carried down with the precipitate. The manganous manganese present is apt to be carried down in this manner, forming salts of the general character $(\text{MnO}_2)_x\text{MnO}$. Less permanganate solution will be used in this case than theory requires. This difficulty is almost entirely overcome by having a considerable amount of zinc sulphate present in the solution. The zinc will then be carried down with the manganese dioxide in preference to the manganous manganese.

451. Determination of Amount of Error.—The extent of the error from this source may be ascertained by a blank determination as follows: A given volume of the permanganate solution, 30 c.c. for instance, is carefully measured out into a beaker and reduced by acidifying with sulphuric acid and adding hydrogen peroxide

in small portions, carefully avoiding excess. The solution is then transferred to a liter flask and neutralized by the addition of zinc oxide. If several grams of zinc have not been used some neutral zinc sulphate should be added. The solution is then diluted to 400 c.c. and warmed to 80°. 19 c.c. of the permanganate solution are then added rapidly and, after vigorous shaking of the flask, the permanganate is added in 0.1-c.c. portions, until a slight excess is present as shown by the pink color of the solution. The solution is vigorously shaken after each addition of permanganate. On standing a few minutes the precipitate settles so that the color of the solution can be seen on holding the flask up to the light.

452. Calculation.—If the reaction proceeded wholly according to the equation



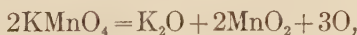
exactly 20 c.c. of the permanganate solution would be required to titrate the manganese obtained from the reduction of 30 c.c. of the same solution. Generally, a little less than 20 c.c. will be used, the deficiency averaging about 1% of the total volume. The volume of the permanganate solution used in a given titration or the value of 1 c.c. in manganese must be increased in the proportion found by the blank determination.

453. Method of Adding the Permanganate Solution.—If the permanganate solution is added in small portions to the solution of the manganous salt the error will be greater than when the total amount of permanganate is added all at once. If the amount of manganese present is entirely unknown one or more preliminary titrations must be made. In the first the permanganate solution is added several cubic centimeters at a time until the end-point has been reached or passed. In the second nearly the total amount of permanganate is added all at once and the end-point reached by the addition of amounts less than a cubic centimeter. In the third titration the total amount of the permanganate solution less a few tenths of a cubic centimeter is added at once and the end-point reached by adding portions of a tenth of a cubic centimeter or less.

454. Interfering Metals.—Of the other metals which occur in manganese ores IRON is most common, but it does not interfere

with the titration of the manganese since it is precipitated on neutralizing the solution with zinc oxide. COPPER is also precipitated by means of the zinc oxide. NICKEL and LEAD, if present, produce high results. The lead may be removed by treating the solution with sulphuric acid or may be removed with cobalt and nickel as sulphides. The solution is neutralized with ammonia and ammonium sulphide added. It is then acidified with hydrochloric acid and filtered from the sulphides of cobalt, nickel, and lead. The hydrogen sulphide is expelled by boiling and the manganese titrated after neutralization of the solution with zinc oxide. CHROMIUM as well as COBALT interferes if present even in small amounts. Manganese may be separated from chromium by precipitation as dioxide from a strong nitric acid solution by means of potassium chlorate. It is filtered off, washed, and, after solution in hydrochloric acid and neutralization with zinc oxide, titrated with the permanganate solution.

455. Strength of Solution.—As the Volhard reaction may be represented as follows, $\text{MnO} + \text{O} = \text{MnO}_2$, one liter of a fifth-normal permanganate solution would be equal to 1/10 of the molecular weight of MnO_2 in grams if the oxygen were evolved from the potassium permanganate in the usual manner. As in the Volhard reaction it decomposes as follows,



a fifth-normal solution has only three-fifths of its usual strength. One liter of the fifth-normal solution is therefore equal to 3/50 of the molecular weight of MnO_2 , i.e., 1 c.c. is equal to .00522 gram of manganese dioxide.

EXERCISE 58.

Determination of Available Oxygen in Pyrolusite.

(a) By Oxalic Acid.

The ore is finely powdered, spread out on a watch-crystal, and dried four to six hours on the water-bath or in an air-bath kept at 100°. Portions weighing 0.870 gram are quickly weighed out and transferred to beakers. Portions of pure recrystallized oxalic acid weighing 1.2605 grams are added to the beakers containing the ore. About 50 c.c. of water and a few cubic centimeters of dilute sulphuric acid are added to each beaker and the solution heated gently until the ore is dissolved. The temperature must not

be allowed to rise above 60° . Without filtering off the insoluble residue, which is generally white, the warm solution is titrated with standard permanganate solution. More dilute sulphuric acid is added if the permanganate color fades slowly or manganese dioxide is precipitated. The percentage of MnO_2 present is found by subtracting the number of cubic centimeters of N/5 potassium permanganate used from 100.

If pure recrystallized oxalic acid is not at hand, the C.P. article may be used. It is tested as follows: One-gram portions of the oxalic acid are weighed out and titrated against the permanganate solution. The amount of oxalic acid which will reduce exactly 100 c.c. of the permanganate solution is then calculated. This amount is then weighed out instead of 1.2605 grams of the pure acid. It is advisable to test even the most carefully prepared article by titration against the permanganate solution used.

(b) *By a Ferrous Salt.*

Determine the percentage of MnO_2 in the same or another sample of pyrolusite as follows: 0.870 gram of the finely powdered and dried material is weighed out and transferred to a 250-c.c. flask. Add a little distilled water and some dilute sulphuric acid and then a gram or two of sodium bicarbonate. Insert a rubber stopper fitted with a bent glass tube dipping into a solution of sodium bicarbonate exactly as used in the standardization of the permanganate solution with iron wire. An amount of ferrous sulphate or of ferrous ammonium sulphate which has been found by titration to be exactly equal to 100 c.c. of the permanganate solution is now added. The solution is warmed gently until no more black particles of the pyrolusite remain undissolved. The excess of ferrous sulphate is titrated with the permanganate solution, a red color permanent for one-half minute being taken as the end-point, both in this titration and in testing the purity of the ferrous salt. The number of cubic centimeters of N/5 permanganate used, subtracted from 100 gives the percentage of MnO_2 present.

EXERCISE 59.

Determination of Manganese in Pyrolusite.

456. *Solution of the Ore.*—1.5 grams of the dried ore are weighed out and digested with 30 c.c. of concentrated hydrochloric acid until no black particles remain or until no further solvent action is noticed. The insoluble residue is filtered off on a small paper, the solution being allowed to flow into a 250-c.c. flask. After washing the paper free from manganese, the residue is fused with sodium and potassium carbonates unless the absence of manganese has been shown by a previous test. The moist paper is thrown into a platinum crucible and burned. Four to six times as much sodium and potassium carbonates are added and the contents of the crucible

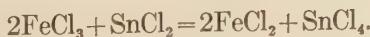
fused. The presence of manganese is generally indicated by the characteristic green color. Whether the fusion is green or not the fused material is dissolved in water, the solution acidified with hydrochloric acid and added to the main solution of the ore.

457. Neutralization of the Solution.—The solution is diluted to the mark and 50-c.c. portions withdrawn with a calibrated pipette. These portions are placed in Florence flasks of 750- to 1000-c.c. capacity. Zinc oxide is added in small portions with vigorous shaking of the flask until the solution is neutral. At this point the iron which is almost invariably present begins to be precipitated as the hydroxide. The precipitation of the iron is hastened by warming the solution. The zinc oxide should be added cautiously until the solution is colorless, indicating the complete precipitation of the iron. A large excess of the zinc oxide should be avoided. If too much has been added, so that the solution is turbid or the precipitate whitish instead of red, it may be removed by the cautious addition of hydrochloric acid. A slight excess of zinc oxide is not disadvantageous.

458. Titration.—The solution is diluted to about 400 c.c., warmed to 80°, and titrated with the permanganate solution, adding 4- or 5-c.c. portions at once and shaking vigorously. After allowing the precipitate to settle a little, the color of the solution can easily be observed. When the characteristic permanganate color has been given to the solution, the titration is interrupted, and to the second flask, after neutralizing, diluting to 400 c.c., and warming, is added the total amount of permanganate solution which was added to the first flask less the final portion which gave the end-point. After thorough shaking, 1-c.c. portions of the permanganate are added until the end-point is reached. To the third flask the total amount of permanganate solution within 1 c.c. is added, and after shaking, the end-point is reached by adding 0.1-c.c. portions of the permanganate solution. The fourth and fifth portions of the solutions are also titrated.

Calculate the per cent of manganese in the ore.

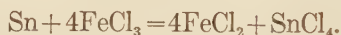
459. Determination of Tin.—Tin may readily be determined volumetrically by titrating the ferrous iron produced by the reduction of ferric chloride by stannous chloride or metallic tin. If the tin is obtained as the *stannous salt*, it is treated with an excess of ferric chloride, when the following reaction takes place:



By determining the amount of ferrous iron produced, the amount of tin present in the stannous condition is found. This determination is of value because the tin salt is frequently used as a reducing agent. Cupric chloride may be used in place of the ferric chloride.

If the tin is in the *metallic* condition it may be dissolved

in hydrochloric acid with exclusion of air and the solution of stannous chloride treated with ferric chloride. The metallic tin may also be treated directly with ferric chloride solution, in which it dissolves readily, especially if it is finely divided. No hydrogen is evolved, but the tin dissolves according to the following equation:



If iron is present in the tin the solution in hydrochloric acid must be allowed to stand twelve hours after the addition of metallic zinc. The tin is completely precipitated and may be removed from the zinc with a brush, washed, dissolved in ferric chloride and the ferrous iron determined. The tin in stannic compounds may be determined in the same manner, the solution of the stannic compound in hydrochloric acid being treated with zinc as directed above.

EXERCISE 60.

Analysis of Stannous Chloride.

Make a solution of ferric chloride by dissolving 60 grams of the commercial salt in a liter of water. One gram of the stannous chloride is weighed out, placed in a beaker, and 50 c.c. of the ferric chloride solution added together with a few cubic centimeters of dilute hydrochloric acid. 50 c.c. of the ferric chloride solution is placed in a similar beaker and the same amount of hydrochloric acid added. When the stannous chloride is dissolved, add a few grams of sodium sulphate and at least 200 c.c. of boiled and cooled distilled water to each beaker and titrate the tin solution with standard permanganate solution until a faint rose color permanent for one-half minute is obtained. Add permanganate to the ferric chloride solution drop by drop until the same color is obtained. The amount of permanganate added to this solution must be subtracted from the amount added to the solution of the tin. Calculate the amount of crystallized stannous chloride, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, present. 1 c.c. N/5 permanganate equals .02259 gram of this salt.

DETERMINATION OF CALCIUM.

460. Titration of Calcium Oxalate.—Calcium may be determined very rapidly and accurately by titrating the oxalic acid in the calcium oxalate precipitate with standard permanganate solution. The calcium may be precipitated in the usual manner by means of ammonium oxalate and digesting the precipitate

until the solution is clear. The precipitate is thoroughly washed with hot water. If it is large it is advisable to wash entirely by decantation. The filter-paper through which the wash-water is passed is treated with a little warm dilute sulphuric acid and then washed with water, allowing the liquid to flow into the beaker containing the bulk of the precipitate. When the precipitate on the filter-paper has been entirely dissolved and washed out, the portion in the beaker is dissolved by gently warming the solution and adding more dilute sulphuric acid if necessary. The oxalic acid is then titrated in the usual manner.

461. Titration of the Excess of Oxalic Acid.—The washing and dissolving of the precipitate may be obviated, if the calcium is precipitated in a measuring-flask of convenient size, by neutralizing with ammonia and adding a measured excess of oxalic acid. For this purpose a standard solution may be used, or the pure crystals may be weighed out. After digesting the precipitate until the solution is clear it is diluted to the mark on the flask with water and after thorough shaking is allowed to settle a few minutes. As the precipitate occupies a small volume a few drops of water should be added after the solution is up to the mark. The exact amount to be added may be found by dividing the weight of the precipitate by its specific gravity.

The solution is filtered through a dry paper and the oxalic acid in a measured volume of the filtrate titrated with standard permanganate solution after acidifying with sulphuric acid. The solution need not be cooled to the room temperature if the portion of the filtrate to be titrated is measured out as soon as filtered. A very convenient method of procedure is to precipitate the calcium in a 500-c.c. flask and after digestion allow to cool somewhat, dilute, and shake. After standing a few minutes the solution is filtered through a dry paper into a 250-c.c. measuring-flask. The solution is allowed to flow into this flask until it is filled to a little above the mark. The excess is taken out with a glass tube used like a pipette. The solution is then poured into a beaker, the flask rinsed out, and the oxalic acid titrated.

When a large number of calcium determinations must be made the volumetric method is convenient and rapid. If only a few need be made it is doubtful if time would be saved.

POTASSIUM DICHROMATE SOLUTION.

462. Conditions of Use.—The use of this substance as an oxidizing solution is limited by the fact that it does not give up its oxygen to many substances which can be oxidized by potassium permanganate or iodine. The titration must always be so conducted that the end-point is obtained by titrating ferrous iron, using potassium ferricyanide as the outside indicator. On the other hand the solution has the advantage that it is very stable, being unaffected by dust or the organic matter which might come in contact with it. It may be used in the Mohr burette, which is closed with a rubber tube and a pinch-cock. Dilute hydrochloric acid is not oxidized as it is by potassium permanganate. The presence of this acid in the solution does not interfere with the titration when carried out cold. Potassium dichromate may also be easily obtained very pure, so that the solution may be made by weighing out the pure salt. Its oxidizing power is considerably increased when used in hot concentrated solution. It differs from potassium permanganate in that under these conditions it does not lose an appreciable amount of oxygen in the free condition.

463. Pure Potassium Dichromate may generally be obtained commercially. Sulphates and chlorides are the common impurities. If the pure salt is not at hand, it may be made by recrystallizing the impure substance. The salt contains no water of crystallization and is not hygroscopic. It may be fused without loss of oxygen, and this method of drying is frequently used. If dust or organic matter is present, the fused salt is reduced. If heated higher than necessary to fuse it, it may lose oxygen. As the salt dried at 100° loses only an inappreciable amount when fused, this method of drying seems to be unnecessary. 9.817 grams of the pure salt are weighed out, dissolved in water and diluted to a liter to make a fifth-normal solution.

464. Standardization by Means of Iron Wire.—The strength of the solution may be verified by standardization with a known amount of iron as directed for the standardization of potassium

permanganate solution. The oxidation of the organic matter in the hydrochloric acid solution of the iron wire by means of potassium chlorate is unnecessary, as the dichromate is not reduced by the hydrocarbons present. The iron wire may therefore be dissolved in dilute sulphuric acid, the air being excluded by means of carbon dioxide by the methods already given. If the standardized solution of ferric chloride is used, it is not advisable to reduce it by means of zinc, as the zinc salts react with the ferricyanide used as the indicator, forming the white zinc salt which obscures the end-point. The reduction by means of stannous chloride solution is well adapted for use when the iron is to be titrated with dichromate solution. The stannous chloride is added cautiously to the hot ferric chloride solution until the characteristic color of the ferric chloride has disappeared. The slight excess of stannous chloride is removed by adding a considerable amount of mercuric chloride solution. After diluting the solution somewhat and adding dilute sulphuric acid the ferrous iron is immediately titrated with the dichromate solution. The reduction with ammonium bisulphite and hydrogen sulphide is carried out exactly as directed for titration with the permanganate solution.

465. Standardization by Means of Pure Ferrous Ammonium Sulphate is carried out in the same manner as when a permanganate solution is standardized with this salt, the end-point of the titration being ascertained by means of potassium ferricyanide. The standardization by means of oxalic acid or oxalates is not available for dichromate solutions, nor is the decomposition by means of hydrogen peroxide and measuring the gas evolved. A potassium permanganate solution which has been carefully standardized by any of these methods may be used as a standard for a dichromate solution, using a ferrous salt to make the comparison. In this case the errors of three titrations would be included in the final result.

466. Analysis of Iron Ores.—When a dichromate solution is used for the determination of the iron in an iron ore, it is decomposed in exactly the same manner as when the iron is titrated with a permanganate solution. Zinc is not used for the reduction, and when stannous chloride is employed, the addition of the phosphoric acid and the manganous sulphate is unnecessary. As

hydrochloric acid is not readily oxidized by potassium dichromate, the solution of iron need not be so thoroughly cooled as when permanganate is used.

EXERCISE 6r.

Preparation of Standard N/5 Potassium Dichromate Solution.

Weigh out 9.817 grams of pure dry potassium dichromate. Dissolve in warm water, transfer the solution to a liter flask, cool, and dilute to the mark.

467. Standardization by Ferrous Ammonium Sulphate.—1.962 grams of the pure salt are weighed out and dissolved in water, dilute sulphuric acid is added, and the solution titrated immediately with the dichromate solution.

468. Indicator.—The potassium ferricyanide solution to be used as the indicator must be made immediately before it is required for use. A crystal about the size of a pea is placed in a small beaker and 75 to 100 c.c. of distilled water added. The solution is most readily withdrawn by means of a short glass tube. A row of single drops are placed by means of this glass tube on a white porcelain plate. On touching one of these drops with a rod dipped in a solution of ferric chloride only a light-brown color should be produced. If any blue color develops, the ferric chloride should be boiled after the addition of a drop or two of nitric acid and the test repeated. If a blue color is still developed, the ferricyanide is contaminated with ferrocyanide and cannot be used. When an indicator has been obtained which is satisfactory, the progress of the titration is ascertained by touching drops of the indicator with drops of the solution taken out on the stirring-rod.

469. Titration.—To avoid loss of ferrous iron, nearly all of the calculated amount of the dichromate solution should be added to the iron solution before a test is made. Two or three drops of the dichromate solution are then added at a time and the test made until only a faint blue color is developed. A drop at a time is then added until the spot test shows no blue color. No change in the color of the spot test can then be noticed on adding more dichromate to the iron solution.

470. The Standardization by Means of Soft-iron Wire in which the percentage of iron has been determined is carried out as follows: Prepare a Bunsen valve as directed on p. 311 and a 250-c.c. Florence flask. Clean some soft-iron wire, in which the percentage of iron has been determined, by rubbing with sandpaper and filter-paper. Make it into a spiral by winding on a lead-pencil. After cleaning do not touch the wire with the fingers. Weigh from 0.25 to 0.3 gram and transfer to the flask. Add about 15 c.c. of dilute sulphuric acid and a gram or two of sodium bicarbonate. Close the flask with the rubber stopper and the Bunsen valve and warm gently until the iron is dissolved. Add cold boiled water until the flask is about half full,

then throw in a gram or two of sodium bicarbonate, and if the solution is not strongly acid, add a few cubic centimeters of dilute sulphuric acid and titrate immediately with the dichromate solution.

EXERCISE 62.

Determination of Iron in an Iron Ore.

To determine the iron in an iron ore, $\frac{1}{2}$ gram of the powdered ore is weighed and dissolved exactly as directed in Exercise 57, page 320. The solution of the iron is reduced by means of stannous chloride. It is heated nearly to boiling and the stannous chloride solution added drop by drop until the color of the solution is a pure green and a slight excess of the stannous chloride is present. Cool the solution by allowing cold water to flow over the flask. 50 c.c. of mercuric-chloride solution is added all at once and the solution vigorously agitated by rotating the flask with the hand. The iron is immediately titrated with the dichromate solution. 1 c.c. of N/5 dichromate solution is equal to .01118 gram of iron, or .01598 gram of ferric oxide. Compute the percentage of metallic iron and also of ferric oxide in the ore.

471. Determination of Chromium in Chrome Iron Ores.—

These ores are most readily decomposed by fusion with an alkaline oxidizing mixture by which the chromium is converted into chromate, which on treatment with water dissolves, leaving the iron as oxide. After destroying the excess of the oxidizing agent, the chromate may be determined by means of a known amount of ferrous iron. The best fusion mixture for this purpose seems to be 4 to 5 parts of sodium hydroxide and 3 to 4 parts of sodium peroxide, or 8 to 10 parts of sodium peroxide alone. The fusion must be conducted in a silver, nickel, or copper crucible, as platinum is strongly attacked by this mixture.

EXERCISE 63.

Determination of Chromium in Chrome Iron Ore.

472. **Decomposition of the Ore.**—Grind the ore in an agate mortar until it is reduced to the finest powder. Weigh out $\frac{1}{2}$ gram and transfer to a nickel or copper crucible. Add 4 to 5 grams of sodium peroxide, being careful to select the yellow material. The white crust on top is sodium carbonate and oxide resulting from decomposition of the peroxide. Mix the material

well with a platinum wire or glass rod. This can be more efficiently done if the peroxide is placed in the crucible first and the ore on top.

Heat at first with a very small flame. After about ten minutes the material should be entirely liquid. It should be kept in this condition for ten or fifteen minutes. Allow to cool until a crust forms on top, add 1 gram of sodium peroxide, and fuse again for about five minutes. After cooling, transfer the crucible to a porcelain dish and dissolve the fused mass in hot water. Take out and rinse the crucible. If the solution is purple, add a little more sodium peroxide. Boil the solution for ten minutes to decompose the sodium peroxide. Filter off and wash thoroughly the insoluble material. Any portion of this material which is not soluble in hydrochloric acid must be fused with a little more sodium peroxide, as it may be undecomposed portions of the ore.

473. Titration of the Chromic Acid.—Acidify the filtrate with dilute sulphuric acid and add an excess of about 15 c.c. Add a weighed amount of ferrous ammonium sulphate which is more than sufficient to reduce the chromium present. The presence of an excess of the ferrous salt may be ascertained by touching a drop of the ferricyanide indicator with a glass rod which has been dipped into the solution. A sufficient amount of the ferrous salt should be placed in a weighing-bottle and carefully weighed. After adding an excess to the chromate solution the residue is weighed. The amount added is found by difference. 5 grams of the ferrous ammonium sulphate will generally be found to be a sufficient amount. The excess of ferrous iron is titrated with standard dichromate solution.

The value of the ferrous salt is ascertained by titrating 2-gram portions with the dichromate solution. Calculate the volume of the dichromate solution equivalent to 5 grams of the ferrous salt or the amount added to the solution of the chrome ore. The difference between this number and the number of cubic centimeters used in titrating the excess of ferrous iron gives the amount of chromate present in the solution of the ore in cubic centimeters of N/5 dichromate solution. Calculate the percentage of Cr_2O_3 in the ore, 1 c.c. of the N/5 dichromate solution being equal to .005073 gram of Cr_2O_3 .

PROBLEMS.

Problem 11. The calcium in $\frac{1}{2}$ gram of a sample of dolomite was precipitated with 1 gram of crystallized oxalic acid and the excess titrated with 34 c.c. of N/5 potassium permanganate solution. Calculate the per cent of calcium oxide in the dolomite. How much dolomite and oxalic acid must be taken so that the per cent of calcium oxide will be given by the number of cubic centimeters of N/5 potassium permanganate?

Problem 12. In the analysis of a sample of stannous chloride, a half-gram portion was treated with ferric chloride solution and titrated with N/5 potassium permanganate solution requiring 20 c.c. The tin in another half-gram portion was weighed as stannic oxide, .330 grams being obtained. Calculate the per cent of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and SnCl_4 present.

CHAPTER XXV.

IODOMETRIC METHODS.

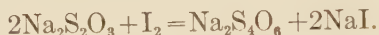
474. Conditions of Use of Iodine Solutions.—Iodometric methods are largely used, and are very accurate on account of the great delicacy of the indicator available, starch solution giving a distinct blue color with a very small amount of free iodine. *Iodine acts as an oxidizing agent in acid and neutral solutions.* The caustic alkalis, as well as solutions of the alkali carbonates, combine with the iodine, rendering titration in such solutions impossible. Sodium or potassium bicarbonate is not acted on by iodine, and as solutions of these salts are alkaline toward all acids stronger than carbonic acid, by working with solutions of these salts, iodine may be used to oxidize many substances which require an alkaline solution. It is therefore possible to use iodine to oxidize a great variety of chemical substances. The solubility of iodine in water solutions of potassium iodide, as well as in alcohol, chloroform, glacial acetic acid, and other organic solvents, still further enlarges its use, since both the iodine and the substance acted on must be in solution.

The use of iodine is somewhat restricted because its solutions are not stable, while many of the methods of standardization are indirect. The volatility of the iodine also introduces difficulties in its use. Iodine solutions must not come in contact with rubber, cork, or other organic material. Paraffine is unacted on.

475. Solvents of Iodine.—The most commonly used solution of iodine is made by dissolving the element in a water solution of potassium iodide. An unstable compound of the formula KI_3 is formed under these circumstances. A considerable excess of potassium iodide must be present in order to dissolve the iodine. Alcoholic solutions of iodine have been largely used for the determination of the so-called iodine number of oils. For this purpose

a solution in glacial acetic acid has recently superseded the alcoholic solutions formerly used.

476. Reducing Solutions.—As many of the methods of standardizing iodine solutions consist in first standardizing a reducing solution, which is then compared with the iodine solution, the reducing solution must always be at hand in iodometric work. The solution most commonly used for this purpose is SODIUM THIOSULPHATE. The iodine is oxidized according to the following equation:



A solution of SODIUM ARSENITE is sometimes used, especially for the titration of bleaching-powder. It reacts with the iodine as follows:



Neither of these solutions is absolutely stable, though more so than the iodine solutions. The most active decomposing influence on the sodium thiosulphate solution seems to be the action of carbon dioxide in the presence of oxygen and sunlight.* The solution should therefore be made by dissolving the thiosulphate in water from which the carbon dioxide has been expelled by boiling. The carbon dioxide may then be excluded from the bottle by means of a soda-lime tube or the solution may be protected from the air by pouring a layer of petroleum-oil over it and siphoning out the solution. Made and protected in one of these ways, the solution will remain unchanged for months.

477. Preparation of Solutions.—Although the commercial resublimed iodine may frequently be obtained free from all impurities except moisture, which may be removed by drying in a desiccator over sulphuric acid, a given sample cannot be relied on until tested. For this purpose a portion is sublimed according to the direction given in Chapter II, p. 34. A solution made from this resublimed iodine may be titrated against a thiosulphate solution, which is then titrated against a solution of a weighed portion of the unpurified iodine dissolved in potassium iodide solution.

The sodium thiosulphate cannot be weighed out exactly because of uncertain hydration, unless it has been recrystallized and care-

* Topf. Zeit. anal. Chem., 26, 150.

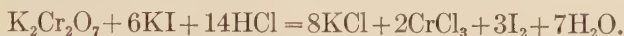
fully dried. A salt may sometimes be obtained in this manner which gives solutions of exact strength.

STANDARDIZATION.

Neither the iodine nor the sodium thiosulphate solution should be relied on without standardization, although if both solutions are made from carefully purified material, and on comparison by titration are found to be of the strength calculated from the weight of material used, they may be employed without further verification, except in the most careful work.

478. Resublimed Iodine.—The thiosulphate solution may be standardized by means of small weighed portions of resublimed iodine. As the iodine is hygroscopic, it should be resublimed immediately before use. The loss by volatilization may also be considerable unless the weighed portions are immediately dissolved in potassium iodide and titrated without delay.

479. Potassium Dichromate, as well as various other oxidizing substances, have been recommended for use in standardizing the thiosulphate solutions. Potassium dichromate can readily be obtained pure. It will liberate a definite amount of iodine from a potassium iodide solution acidified with hydrochloric acid. The reaction takes place according to the following equation:



A sufficient amount of potassium iodide must be present to dissolve the iodine liberated, which is then titrated with the thiosulphate solution. The decomposition of the potassium dichromate is not complete unless the potassium iodide, as well as the hydrochloric acid, is present in considerable excess. If a sufficient amount of hydrochloric acid is not present, the blue starch iodide color will reappear on adding more hydrochloric acid after titrating the iodine with the thiosulphate solution. The following proportions will generally be found satisfactory: To 10 c.c. of fifth-normal potassium-dichromate solution, 10 c.c. of a 10 per cent potassium-iodide solution and 5 c.c. of strong hydrochloric acid is added. On account of the volatility of the iodine, it is advisable to carry out the operation in a glass-stoppered bottle.

480. Potassium Permanganate reacts more readily with the hydriodic acid. If a standard solution is at hand, a measured

volume may be added to a solution of potassium iodide acidified with hydrochloric acid and the iodine liberated titrated at once. The decomposition takes place according to the following equation:



481. The Iodates of Potassium and Sodium have also been recommended for use in a similar manner. They are decomposed by hydriodic acid instantly and completely. The acid potassium iodate is very readily obtained in a high state of purity. This salt has the disadvantage of being sparingly soluble in water, and on account of the large percentage of available oxygen the quantities to be weighed out are small, necessitating very careful weighing. If a large amount is weighed out, the solution must be made up to a definite volume and portions measured out. The decomposition takes place according to the following equation:



482. Barium Thiosulphate.—The iodine solution is standardized by titration with a sodium thiosulphate solution which has been standardized by one of the methods already given. It may be directly standardized by the titration of a weighed amount of pure barium thiosulphate. This salt may be made by mixing together a warm solution of 50 grams of sodium thiosulphate in 300 c.c. of water and 40 grams of barium chloride dissolved in the same amount of water. The solution should be stirred vigorously while the salt crystallizes out. It is filtered off, washed with water until free from chlorides, and dried in the air. It contains one molecule of water of crystallization, its formula being $\text{BaS}_2\text{O}_3 \cdot \text{H}_2\text{O}$. It is very sparingly soluble in water, a solution made by shaking an excess of the salt with water at 17.5° for fifteen minutes being exactly N/100 in strength. Because of its high molecular weight careful weighing is unnecessary. Quantities weighed out for the standardization of iodine solutions are treated with water in a beaker. Because of the slight solubility of the salt, the iodine solution is added to the beaker while undissolved thiosulphate still remains. When all or nearly all of the salt is dissolved, starch solution is added and the addition of the iodine solution continued until a permanent blue color is produced.

483. Pure Arsenious Oxide may also be used for the standardization of iodine solutions. Weighed portions are dissolved in sodium bicarbonate solution, and after the addition of starch solution the iodine is added until the end-point is reached.

484. The Starch Solution is made by placing a gram or two of starch in a porcelain mortar, adding a little water, and grinding to a smooth paste. 150 or 200 c.c. of boiling water are then poured into the mortar while stirring continually with the pestle. The solution is then poured into a beaker containing an equal volume of cold distilled water. After the solution has been allowed to stand and settle for some time, the clear liquid is decanted for use. This starch solution is sensitive only when fresh and must be prepared each day. If saturated with sodium chloride, or a few drops of chloroform added, it keeps much longer. Various other methods of making a permanent starch solution have been suggested, but the solution made fresh each day seems to be the most satisfactory.

If the starch is added to a solution containing a considerable amount of free iodine, a compound of starch and iodine is produced which is decomposed very slowly by the thiosulphate. The indicator is therefore added only when nearly all of the free iodine has been removed by the sodium thiosulphate. Potassium iodide as well as free iodine must be present to produce the blue color with starch. As solutions of potassium iodide are not stable, this salt must be kept in the solid form and only freshly made solutions used.

EXERCISE 64.

Preparation and Standardization of N/10 Iodine and Sodium Thiosulphate Solutions.

485. Sodium Thiosulphate Solution.—If recrystallized and carefully dried sodium thiosulphate is at hand, weigh out carefully 24.83 grams, dissolve in water, and dilute the solution to a liter. If the ordinary C.P. salt is used, weigh out about 25 grams for a liter of solution. In either case use distilled water which has been thoroughly boiled to expel the carbon dioxide and place the solution in a bottle, through the stopper of which a siphon passes for withdrawing the solution. Pour enough naphtha over the solution to form a layer about 1 cm. deep, or put a straight calcium chloride tube in the second hole of the stopper. Fill the tube with fresh soda-lime.

486. Iodine Solution.—Weigh 12.697 grams of recently sublimed iodine in a weighing-bottle. Keep the stopper tightly closed, except when putting in or taking out iodine. Only glass, porcelain, or platinum should come in contact with the iodine. Be careful not to spill crystals on the balance-pan or in the case. About 18 grams of pure potassium iodide are weighed out and dissolved in about 150 c.c. of water. The potassium iodide should be tested by dissolving about 1 gram in 10 c.c. of water and acidifying with dilute hydrochloric acid. The solution must be colorless and remain so on the addition of a few cubic centimeters of starch solution.

The iodine is transferred to a liter flask by removing the stopper of the weighing-bottle and inserting the bottle into the neck of the flask, which for this purpose is held in a horizontal position. On raising the flask to an upright position and tapping the weighing-bottle, the bulk of the iodine will be transferred to the flask. The few remaining crystals are removed by adding a little of the potassium iodide solution and shaking the stoppered weighing-bottle until dissolved. The solution is poured into the flask and the weighing-bottle and stopper are thoroughly rinsed with the potassium iodide solution. The remainder of this solution is added to the liter flask, which is stoppered, and shaken at intervals until all of the iodine is dissolved. If the last of the iodine crystals dissolve slowly, a few crystals of potassium iodide may be dropped into the flask and the concentrated solution formed left undisturbed in contact with the iodine crystals. The solution may also be very gently warmed on the water-bath.

487. Comparison of Iodine and Sodium Thiosulphate Solutions.—When all of the iodine has been dissolved, the solution is diluted to the mark and transferred to a glass-stoppered bottle, which is best kept in a cool, dark place. The solution is immediately compared with the sodium thiosulphate solution. 25 c.c. of iodine solution is measured out into a beaker and the thiosulphate solution added until the color has been almost entirely removed, leaving the solution a light yellow. A few cubic centimeters of the starch solution are then added and the addition of the thiosulphate solution continued until the intense-blue color is just removed. Until experience is gained, it is advisable to add iodine solution drop by drop until the blue color is restored before reading the burette. There is some danger of overstepping the mark when the end-point is obtained by removing the blue color with the thiosulphate solution.

STANDARDIZATION OF THE SOLUTIONS.

488. First Method. Barium Thiosulphate.—Weigh out several portions of pure barium thiosulphate of about $\frac{3}{4}$ gram. If exactly 0.6688-gram portions are weighed, each will be equal to 25 c.c. of tenth-normal iodine solution. Transfer the portions to beakers and add from 50 to 100 c.c. of water. Without waiting for the salt to dissolve completely, add the iodine solution

slowly with constant stirring until nearly all of the thiosulphate is dissolved. Starch solution is then added and then iodine solution until a slight permanent blue color is produced.

489. Second Method. Arsenious Oxide.—Weigh out 4.95 grams of pure arsenious oxide. Place in a beaker and add about 13 grams of caustic soda. Dissolve in 50 c.c. of distilled water, transfer to a liter flask, and saturate the solution with carbon dioxide. At first the delivery-tube must not be immersed in the liquid, as the latter might be sucked up the tube by the complete absorption of the gas. When the gas-bubbles pass through the liquid undiminished in size, the latter is saturated. Rinse the delivery-tube and dilute the solution to the mark. This solution will be exactly decinormal. Titrate 25-c.c. portions with the iodine solution.

490. Third Method. Acid Potassium Iodate.—Weigh out 0.3251 gram of acid potassium iodate. Dissolve in 50 c.c. of water, heating gently if necessary. Transfer the solution to a 100-c.c. flask, rinsing the beaker carefully, and dilute to the mark. This solution will be exactly decinormal. Measure out 25 c.c. into a beaker, add about 1 gram of potassium iodide dissolved in a little water and a few cubic centimeters of dilute hydrochloric acid. Titrate immediately with the thiosulphate solution.

491. Fourth Method. Resublimed Iodine.—Weigh out about 0.3 gram of recently sublimed iodine, using a tightly stoppered weighing-bottle. Add 10 c.c. of a 10% solution of potassium iodide and shake until the iodine is completely dissolved. Transfer the solution to a beaker and rinse out the weighing-bottle with water and, if necessary, a little potassium iodide solution. Titrate immediately with the thiosulphate solution.

492. Calculation of the Results.—The iodine solution, having been made from pure iodine, must be considered exactly tenth-normal when made, unless some iodine was known to be lost. The titration of the thiosulphate solution immediately after the iodine solution was made is considered as a standardization of the former and is so calculated. The average of the titrations which agreed within less than 0.2 or at most 0.3% is taken. If duplicate titrations agreeing within this limit are not readily obtained, some error is being made in the work, which must be discovered by varying the method of procedure. If, for instance, 24.05 c.c. of the thiosulphate solution is found to be equal to 25 c.c. of the iodine solution, the strength of the solutions being inversely as the number of cubic centimeters of each used, the strength of the thiosulphate solution will be given by the following proportion: $24.05 : 25.00 :: 0.1N : x$. $x = .10395N$.

By the first method of standardization the iodine solution is compared with a weighed amount of barium thiosulphate, which is exactly equal to 25 c.c. of tenth-normal solution. By the same proportion as given above, the strength of the iodine solution may be computed. If, for instance, an average of 24.95 c.c. of iodine solution were used, the iodine solution is .1002N by the proportion $24.95 : 25.00 :: 0.1N : x$. As this value differs

from tenth-normal by only 0.2%, the iodine solution is considered tenth-normal, since the errors of titration may amount to 0.2%.

The results of the second method of standardization are calculated in the same manner. The third as well as the fourth methods being direct standardizations of the thiosulphate solution, its strength is calculated from the results.

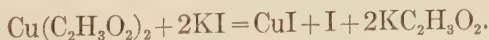
If several days have elapsed between the standardization of the thiosulphate solution and its comparison with the iodine solution this comparison must be repeated. The average of the values found for the thiosulphate solution is taken and used in the proportion when calculating the strength of the iodine solution. If, for instance, 25.18 c.c. of the iodine solution was found to be equal to 24.12 c.c. of the thiosulphate solution, and the average strength of this solution to be .1039N, the proportion will be $25.18 : 24.12 :: .1039 : x$, from which x , or the strength of the iodine solution, will be .09952N.

493. Analysis of Reducing Agents.—All substances which may be analyzed by iodometric methods may be divided into *two classes*, according to whether they act as *reducing agents towards iodine* or as *oxidizing agents towards hydriodic acid*. The reducing agents are analyzed either by titrating directly with standard iodine solution, or by adding an excess of the iodine solution and titrating back with standard thiosulphate solution. The method of titrating a THIOSULPHATE or ARSENIOUS OXIDE has already been given in the methods of standardization. *Antimonous oxide* may be titrated in exactly the same manner as arsenious oxide, tartaric acid or cream of tartar being used to dissolve the antimonous oxide. The titration of a SULPHITE will be given in Exercise 66, page 346. The SULPHIDES, which may be completely decomposed with liberation of hydrogen sulphide, may be analyzed in a similar manner, the hydrogen sulphide being passed through excess of standard iodine solution. The following reaction takes place: $H_2S + I_2 = 2HI + S$. The amount of unreduced iodine is then determined. Easily decomposed sulphides, such as those of cadmium and zinc, the alkali sulphides, and hydrogen sulphide water, are completely decomposed by adding dilute acid and iodine solution. Other reducing substances which can be determined iodometrically are ANTIMONY OXIDE, ALKALI CYANIDES, STANNOUS CHLORIDE, and OILS and FATS, as will be given in the chapter on this subject.

494. Oxidizing Substances, on the contrary, are treated with an excess of potassium iodide, and the solution acidified. The hydriodic acid formed is oxidized to iodine, which combines with the excess of potassium iodide and is then titrated with standard thiosulphate solution. The standardization of the thiosulphate solution by means of ACID POTASSIUM IODATE is an illustration of this method. In this manner FREE CHLORINE, BROMINE, HYPOCHLORITES, BROMATES, FERRIC CHLORIDE, NITROUS ACID, HYDROGEN PEROXIDE, and PERSULPHURIC ACID may be analyzed. Oxidizing substances decomposed with difficulty, such as CHLORATES, CHROMATES, and minerals containing MANGANESE DIOXIDE, may be analyzed by treatment with concentrated hydrochloric acid and distillation of the chlorine which is absorbed in potassium iodide solution. The iodine liberated is then titrated with standard thiosulphate solution.

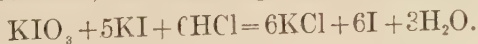
495. Antimony may be determined by first oxidizing with potassium chlorate (1 gram) in strong hydrochloric-acid solution. The excess of chlorine is boiled out, the solution cooled, and excess of potassium iodide added (1 gram). The antimony is reduced from Sb_2Cl_5 to Sb_2Cl_3 with liberation of iodine which is titrated with thiosulphate solution. Copper and iron must be absent from the solution.

496. Copper may be determined in a similar manner. The nitric-acid solution of the copper is neutralized with ammonia or sodium carbonate and then acidified with acetic acid. Ten c.c. of a 10 per cent solution of potassium iodide is added to the copper solution, which should not exceed 15 c.c. in volume. Iodine is liberated according to the following reaction:



The iodine liberated is titrated with sodium-thiosulphate solution. Lead, bismuth, arsenic, antimony, and iron should be absent from the solution.

497. Acids may also be determined iodometrically by using a solution of potassium iodate and potassium iodide in the proportion of 1 atom of the former to 5 atoms of the latter. On acidifying such a solution, the following reaction takes place:



By titrating the iodine liberated, the amount of acid added may be computed, since 1 atom of iodine is liberated by 1 molecule of a monobasic acid. Bases may also be determined by adding an excess of acid and titrating the iodine liberated after addition of the iodate and iodide solution. In this manner the extremely sensitive indicator of iodometric titrations may be used in acid titrations. Although in this manner a much sharper end-point may be obtained than by the use of the ordinary indicators for acids and bases, the accuracy of a given titration will be no greater unless the measurement of volumes and the purification of reagents is carried out with the same high degree of accuracy.

498. Bunsen's Distillation Apparatus. — For carrying on the distillation of the chlorine from oxidizing agents, such as manganese dioxide, various forms of apparatus have been devised. One of the best is that of Bunsen, shown in Fig. 57. The oxidizing

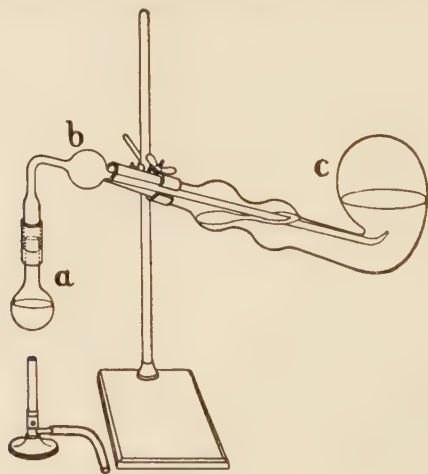


FIG. 57.

substance to be analyzed is placed in the small bulb *a*, which is connected with the tube *b* by means of a ground-glass joint over which a rubber tube of suitable size is stretched. This joint must be tight, so as to prevent loss of chlorine, which must not, however, be allowed to come in contact with the rubber. The receiver *c* is half filled with 10% potassium iodide solution, which is decomposed by the chlorine with liberation of iodine. The chlorine is driven out of the flask *a* and the tube *b* with the excess of hydrochloric acid and the steam produced by boiling the solution. A

slow stream of carbon dioxide may be produced by placing a few pieces of magnesite in the flask *a*. This is not necessary, however.

499. Mohr's Distillation Apparatus.—Another form of apparatus which was devised by Mohr is shown in Fig. 58. In this apparatus the joints are made by cork stoppers coated with paraffine, which

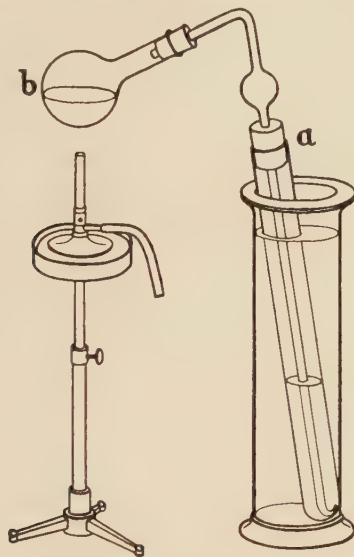


FIG. 58.

is not acted on by chlorine. The receiver is a tube about 30 cm. long and 3 cm. wide, which is immersed in a cylinder filled with cold water. The distillation-flask *b* should have a capacity of 50 to 75 c.c.

EXERCISE 65.

Determination of Available Oxygen in Pyrolusite.

Weigh out between 0.2 and 0.25 gram of the finely powdered pyrolusite and introduce into the distillation-flask of either of the forms of apparatus already described. Use a small glass tube for introducing the ore into the flask, obtaining the weight of the material by weighing the tube before and after introducing the ore. About 1.5 grams of potassium iodide are dissolved in 50 c.c. of distilled water and placed in the receiver, which must be kept cool by immersion in ice-water. 20 to 30 c.c. of concentrated hydrochloric acid are introduced into the distillation-flask, which is immediately connected with the delivery-tube and the latter immersed in the potassium

iodide solution. The paraffine-coated cork at *a* is loosely inserted into the receiver.

The distillation-flask *b* is now gently heated until the manganese dioxide is completely dissolved, leaving a white residue which is not affected by further digestion. The solution is finally brought to a boil, and while the Fansen burner is still under the distillation-flask, the delivery-tube is withdrawn from the receiver and rinsed with distilled water. The iodine solution is transferred to an Erlenmeyer flask and the receiver washed with water. A few cubic centimeters of potassium iodide solution are placed in the receiver, into which the delivery-tube is again passed, and the contents of the distillation-flask again boiled for a few minutes. If no more iodine is liberated in the potassium iodide solution, the decomposition of the manganese dioxide is complete, otherwise the distillation must be continued for some time, the contents of the receiver being finally added to the main solution.

The iodine liberated is titrated with standard thiosulphate solution. 1 c.c. of N/10 sodium thiosulphate is equal to .004350 gram of MnO_2 or .003545 gram of chlorine. Compute the percentage of MnO_2 as well as the percentage of chlorine liberated.

EXERCISE 66.

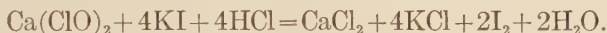
Determination of Sulphur Dioxide in Sodium Sulphite.

Weigh out 1 gram of the sulphite and place in an Erlenmeyer flask. Add 100 c.c. of N/10 iodine solution all at once. It is advisable to measure out the iodine solution with a pipette or a burette into a small beaker. The solution may then be poured from the beaker into the flask. Shake the flask until the salt is dissolved. Rinse the remainder of the iodine solution in the beaker into the flask and titrate the excess with standard thiosulphate solution. 1 c.c. of N/10 iodine solution is equal to .003203 gram of SO_2 or .01261 gram of $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$. Compute the percentage of sulphur dioxide and also of the crystallized salt.

500. The Active Substance in Bleaching-powder is calcium oxychloride $\text{Cl}-\text{Ca}-\text{O}-\text{Cl}$. On adding water, this compound is decomposed into calcium chloride and calcium hypochlorite, $\text{Ca}(\text{ClO})_2$. The value of the bleaching-powder depends on the amount of hypochlorite present. The result of an analysis is usually expressed in percentage by weight of *available chlorine*, although in France it is customary to report the analysis in terms of the number of liters of chlorine gas measured at 0° and 760 mm., which may be obtained from 1 kilogram of the bleaching-powder.

501. Sample.—The analysis may be carried out by a large number of methods, of which two of the most largely used will be given. In order to secure a fair sample, a considerable amount is weighed out and dissolved in a definite volume of water. Measured portions of this solution are taken for analysis. While calcium hypochlorite is quite soluble, bleaching-powder contains a considerable amount of insoluble material. Even when the bleaching-powder is ground to a smooth paste with water, the insoluble material always contains some bleaching material. The insoluble material is, therefore, not filtered off, but is shaken up when portions are measured out. A pipette should be used for this purpose, so as to obtain a fair proportion of the insoluble material.

502. Iodometric Titration.—The amount of available chlorine may be estimated by adding potassium iodide to a portion of the solution of the bleaching-powder and acidifying. The following reaction takes place:



As some calcium chlorate is usually present, the solution is not made strongly acid, as chlorine would in that case be produced by the decomposition of this salt. For this reason, if hydrochloric acid is employed, it is added in very slight excess. The difficulty is entirely obviated by the use of acetic acid. The iodine liberated is then titrated by means of sodium thiosulphate solution.

503. Titration with Sodium Arsenite.—The hypochlorite may also be titrated directly with sodium arsenite solution. To ascertain the end-point drops of the solution are touched to starch-iodide paper. When the hypochlorite is entirely decomposed, the starch-iodide paper is no longer made blue.

EXERCISE 67.

Determination of Available Chlorine in Bleaching-powder.

504. Solution.—Weigh out 7.091 grams of bleaching-powder. As the material is hygroscopic, and also loses chlorine, a weighing-bottle must be used. Transfer the material to a clean porcelain mortar and grind to a smooth paste with the addition of a little water. Add about 75 c.c. of water, mix thoroughly with the pestle, allow to settle a few minutes, and

decant into a liter flask, leaving the bulk of the bleaching-powder in the mortar. Repeat this operation until all of the material has been transferred to the liter flask, which is then filled to the mark with distilled water.

505. Iodometric Titration.—The solution is thoroughly shaken and 50-c.c. portions of the milky liquid are measured out with a pipette and transferred to beakers. About 1 gram of potassium iodide dissolved in a little water is added to one of the beakers. The solution is acidified with acetic acid and the iodine liberated titrated with N/10 sodium thiosulphate solution. Duplicate determinations with the other portions are made in the same manner. 1 c.c. of the tenth-normal thiosulphate solution is equal to .003545 gram of chlorine. If exactly 7.091* grams of the bleaching-powder was weighed out, the number of cubic centimeters of N/10 thiosulphate solution used will be equal to the percentage of available chlorine in the bleaching-powder.

506. Titration with Sodium Arsenite.—50-c.c. portions of the solution of bleaching-powder may also be titrated with the sodium arsenite solution made for standardizing the iodine solution (page 341). **STARCH-IODIDE PAPER** may be made as follows: One gram of starch is ground to a paste with a little water and 100 c.c. of boiling water added with stirring. The solution is filtered and to the filtrate 0.1 gram of potassium iodide is added. Strips of filter-paper are dipped in this solution and dried at 40° to 50°. Strips of this paper are moistened with distilled water and laid on a porcelain or glass plate. Nearly all the sodium arsenite solution thought necessary is added to the solution of the bleaching-powder. After stirring thoroughly, a drop is taken out and touched to the test paper. The depth of the color indicates the amount of arsenite solution still to be added. When considerable hypochlorite is still present, the spot becomes almost black and then colorless again as the iodine is converted into the trichloride ICl_3 . Several cubic centimeters of the arsenite solution should then be added. When the spot test is only light blue, the arsenite solution should be added by drops until the blue color has entirely disappeared. The calculation is made in the same manner as with the iodine solution.

PROBLEM.

Problem 13. A mixture of crystallized sodium thiosulphate, sodium sulphite, and sodium sulphate was analyzed in the following manner: A gram portion was dissolved in water and titrated with N/10 iodine solution, 49 c.c. being required. The hydriodic acid in this solution was then titrated with N/5 sodium-hydroxide solution, 9.5 c.c. being required. The total amount of sulphur in a half-gram portion was then determined as barium sulphate, of which .821 grams was obtained. Calculate the amount of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$, and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ present in the mixture.

* Note for student: Show how this figure is obtained.

PRECIPITATION METHODS.

CHAPTER XXVI.

DETERMINATION OF CHLORIDES, CYANIDES, AND SILVER.

507. Theory of Indicators.—In the volumetric methods already discussed the products of the reactions have been soluble, and the end-point has been obtained by the action of a slight excess of one of the reagents on the indicator.

In ACIDIMETRY and ALKALIMETRY the indicator is either an *acid* or a *base*, but possessing such a *weak chemical affinity* that it cannot remain combined until an excess of the appropriate reagent (base or acid) is present. METHYL ORANGE, for instance, is a weak acid having a bright-red color, while its salts are light yellow. If methyl orange is added to a solution containing a free base, the salt of methyl orange and the base will be formed and the yellow color of the salt will be given to the solution. If carbon dioxide in excess is added to this solution, the color remains yellow because the carbonic acid formed is weaker than the methyl-orange acid, and is therefore unable to displace the latter from its combination with the base. If a strong acid like hydrochloric is added to the solution, it remains yellow as long as there is more base present than can combine with the hydrochloric acid added. When a slight excess of the strong acid has been added, the base combined with the weakly acidic methyl orange is taken by the strong acid. The free methyl orange then gives the reddish color to the solution.

In PRECIPITATION METHODS, on the other hand, advantage is most frequently taken of the *relative solubilities* of the salts of a metal to obtain the end-point. The colored salt which indicates the end of a reaction must be a soluble compound, while the element to be determined must form an insoluble compound.

508. Silver Chromate as Indicator.—In the determination of chlorides by means of silver nitrate solution, a little neutral potassium chromate is added to the solution. On adding the silver nitrate solution the silver is precipitated as silver chloride. When enough silver nitrate has been added to precipitate all of the chlorine, the red silver chromate is formed, which indicates the end of the reaction. As long as chlorides exist in the solution, any silver chromate formed will be decomposed, since if any of this salt is present, it will tend to keep the solution saturated, and any silver which goes into solution as chromate will be immediately precipitated as chloride because of the insolubility of the latter salt. Only when chlorides are absent from the solution can silver chromate be permanently formed. As the silver chromate is decomposed by even a small amount of free acid, the solution must be neutral or slightly alkaline with sodium carbonate.

509. Ferric Sulphocyanate as Indicator.—Silver also forms an insoluble salt with sulphocyanic acid. This acid produces an intensely red color with solutions of ferric iron. The titration of silver is conducted by adding a standard solution of the sulphocyanate to the silver solution containing some ferric sulphate or nitrate. As long as silver is present in the solution the sulphocyanic acid is precipitated, so that the iron compound which is soluble cannot exist. When all of the silver has been precipitated, the next drop of the sulphocyanate solution forms a little of the red ferric compound which indicates the end of the reaction. As the silver sulphocyanate is insoluble in dilute acids, and the ferric sulphocyanate is readily formed under these conditions, the titration may be carried on in acid solutions. The titration of chlorides in acid solution may also be carried out by this method which is known as VOLHARD'S. A measured amount of silver nitrate solution which is more than sufficient to precipitate the chloride present is added to the solution. After the addition of some ferric iron as indicator, the excess of silver is titrated back with standard sulphocyanate solution. Because of the solubility of silver chloride in solutions of the thiocyanates, this method does not give absolutely correct results unless the silver chloride is filtered off and the excess of silver determined in the filtrate.

510. Silver Chloride as Indicator.—Chlorides may also be titrated with silver nitrate solution without the addition of an indicator. After each addition of silver nitrate the solution is thoroughly shaken. The silver chloride readily collects so as to leave a clear solution in which the formation of a white precipitate on the addition of another drop of silver nitrate may readily be observed. The silver chloride does not collect readily unless a considerable amount of chloride is present and the volume of the solution is not too large.

511. Titration of Cyanides.—The alkali cyanides may be titrated with a silver nitrate solution in the same manner as chlorides, the end-point being obtained when no more precipitate is formed. The reaction takes place in two stages as represented by the following equations:



Until one-half of the cyanide has been converted into the silver salt, any precipitate of silver cyanide which forms is dissolved by the undecomposed cyanide on stirring the solution. When the reaction represented by the first equation is completed, further addition of silver nitrate forms a permanent precipitate of silver cyanide according to the second equation. The precipitate readily collects in flocks on vigorously stirring the solution, leaving a clear liquid in which the absence of a precipitate on the addition of a drop of silver nitrate may be readily observed and serves to indicate the end-point.

This titration may also be conducted so that the reaction represented by the first equation is carried out. The silver solution is added until a slight permanent precipitate is formed. If CHLORIDES are present in the alkali cyanides, as is frequently the case, silver chloride will be precipitated in preference to the silver cyanide because of the greater insolubility of the former. The silver chloride reacts with the alkali cyanide as follows:



When all of the cyanide has been converted into the double cyanide of silver and potassium, the next drop of silver nitrate produces a permanent white precipitate. If chlorides are present, this precipitate will be silver chloride, thus forming a more delicate indicator than the more soluble silver cyanide. The amount of cyanide present will also be correctly determined, as is evident from the equation given. If the titration is carried to the second stage, the presence of the chloride introduces an error, as all the chloride combines with silver before the end-point is reached. The amount of chloride present may be determined by noting the volume of silver nitrate solution required for the completion of each stage of the titration. The excess of the silver nitrate required for the second part of the titration is that necessary to precipitate the chloride.

512. Strength of Solutions.—The standard solutions used in precipitation methods may be made according to the normal system, a gram molecular weight of silver nitrate, sodium chloride, etc., being dissolved in a liter of a normal solution. Such solutions are convenient for use when several substances must be titrated with the same standard solution. When a solution is to be used exclusively for the titration of a given substance, it is more convenient to make it of such strength that 1 c.c. is equal to an amount of the given substance which can be represented by a simple number. If a silver nitrate solution is made of such a strength that 1 c.c. is equal to 1 mg. of chlorine, the number of cubic centimeters of silver nitrate solution used to titrate the chlorine in 1 gram of a given substance will give the per cent of chlorine if divided by 10.

513. Standard Silver Nitrate Solutions are made by dissolving weighed amounts of the crystals and diluting to the required volume. The salt may be purchased in very pure condition, seldom requiring drying even. As pure metallic silver may also be readily obtained the standard solutions are sometimes made by weighing out the pure metal and dissolving in nitric acid. If a neutral solution is required, the excess of nitric acid may be removed by evaporation to dryness on the water-bath. The last traces of acid are removed by moistening with water several times and evaporating to dryness on the water-bath. If protected from

the sunlight and contact with organic matter, solutions of silver nitrate retain their strength for a considerable time unless very dilute.

514. Standardization.—Solutions of silver nitrate may be standardized by titration against weighed amounts of pure sodium chloride prepared as directed in Exercise 6. A saturated solution of potassium chromate is used as the indicator. 4 to 5 drops of the chromate solution are added to the solution to be titrated, the volume of which should not be large. The detection of the first faint tinge of red in the yellow chromate solution offers some difficulties. It is more readily done by gaslight than by sunlight because of the yellow tinge of the former. By daylight the red tinge is more readily detected by a comparison of the color of the solution being titrated, with the color of a solution previously titrated from which the red color has been removed by the addition of a pinch of sodium chloride. The red color is also made more pronounced by looking at the solution through a layer of water tinted with chromate to the same color as the solution to be titrated. It is also advantageous to carry out the titration in a porcelain dish, thus giving a white surface for comparison.

515. Indirect Determinations by Means of Standard Silver Nitrate.—Besides the determination of chlorides, this method may be used to determine indirectly all substances which can be converted into neutral chlorides by treatment with hydrochloric acid and evaporation to dryness to expel the excess of hydrochloric acid. The carbonates of the alkalies and the alkaline earths may be treated in this manner to determine the base, and in cases where only the normal carbonate can be present, carbon dioxide may be determined in this manner. The nitrates also of these metals may be converted into chlorides by a similar treatment and determined.

516. Determination of Sodium and Potassium in the Mixed Chlorides.—The amount of potassium and sodium present in a mixture of the chlorides of these metals may be ascertained by a determination of the amount of chlorine present, the weight of the mixed chlorides having first been found. An indirect determination of this kind gives good results only when there is a considerable difference in the atomic weights of the elements, and a large precipitate is weighed. The method is not accurate for a

small amount of one element in the presence of a large amount of the other. The weight of sodium chloride in the mixture is calculated by multiplying the amount of chlorine found by 2.1032,

$$\left(\frac{\text{Molecular weight KCl}}{\text{Atomic weight Cl}} \right),$$

deducting from the product the combined weight of the chlorides and multiplying the remainder by 3.6426:

$$\left(\frac{\text{Mol. wt. NaCl}}{\text{Mol. wt. KCl} - \text{Mol. wt. NaCl}} \right).$$

In multiplying the weight of chlorine found by 2.1032, the amount of potassium chloride is found which would be obtained if this salt alone were present. If this product is the same as the weight of the mixed chlorides, only potassium can be present.

EXERCISE 68.

Determination of Cyanogen in Potassium Cyanide.

In order to secure a fair sample of the material, weigh out 5 grams of the potassium cyanide selected from various parts of the stock to be examined. Dissolve in water and dilute to 500 c.c. Withdraw 50-c.c. portions for titration. If a pipette is used for this purpose, a loose plug of cotton moistened with silver nitrate solution should be placed in the upper part of the stem, and great care should be taken not to draw any of the solution into the mouth.

The silver nitrate solution is made by weighing out 17 grams of the pure dry crystals, dissolving in water, and diluting to 1 liter. It is advisable to test the distilled water for chloride before adding it to the silver nitrate. Pour the solution into a glass-stoppered bottle and keep in the dark. The 50-c.c. portions of the cyanide solution are diluted with an equal volume of water and the silver-nitrate solution added with constant stirring until a slight permanent opalescence is obtained. 1 c.c. N/10 silver nitrate solution is equal to .01304 gram of potassium cyanide. As commercial potassium cyanide is frequently contaminated with sodium cyanide, the percentage of potassium cyanide found may be greater than 100%. This will not occur if the result is given in percentage of cyanogen. 1 c.c. of N/10 silver nitrate solution is equal to .005208 gram of cyanogen.

517. Determination of Silver in Alloys.—The silver in alloys can very readily be titrated by the VOLHARD METHOD, since the presence of a considerable amount of free nitric acid does not dissolve the silver sulphocyanate. Nitrous acid must be absent, however, and that produced by dissolving the alloy must be entirely expelled by boiling the solution. The amount of copper present must not exceed 70%. Alloys in which the percentage of copper is higher, may be analyzed by adding an accurately measured volume of standard silver solution or an accurately weighed amount of the pure metal, so that the ratio of copper to silver shall not exceed 7 to 3. Mercury must be removed by ignition. Arsenic, antimony, cadmium, lead, bismuth, tin, and zinc do not interfere with the titration. Cobalt and nickel interfere because of the color of their nitrates.

EXERCISE 69.

Determination of Silver in a Coin by Volhard's Method.

Weigh out 7.5 to 8 grams of ammonium sulphocyanate, dissolve in water, and dilute to 1 liter. Standardize the solution by titration against the tenth-normal silver solution prepared for Exercise 68. Measure out into a beaker 30 to 40 c.c. of the standard silver solution, dilute with 100 to 200 c.c. of water, and add 5 c.c. of a cold saturated solution of ferric alum. The ferric iron solution must be free from chlorine, and if turbid, a few cubic centimeters of dilute nitric acid may be added. Place the beaker containing the silver on a white surface and add the sulphocyanate solution with constant stirring until a faint permanent reddish tinge is given to the solution. Repeat the titration until duplicates are obtained. As the sulphocyanate solution is permanent, it is advisable to dilute it to exact strength. When it is used to determine silver, it is most convenient to dilute it to such a strength that 1 c.c. will be equal to exactly .010 gram of silver. Having found, for instance, that 30 c.c. of the sulphocyanate solution is equal to 32 c.c. of the N/10 silver nitrate solution, the amount of silver equivalent to the 30 c.c. of the sulphocyanate solution is found by multiplying 32 by .010793, which gives .3454 gram of silver. As it is desired to dilute the solution so that 30 c.c. shall be equal to .300 gram, the volume to be diluted to 1000 c.c. is found by the proportion

$$.300 : .3454 :: x : 1000.$$

As $x = 868.58$, this number of cubic centimeters is diluted to 1 liter. The strength of the solution after dilution is verified by again titrating against the standard silver solution.

Thoroughly clean a dime or other silver coin by rubbing with alcohol ammonia, etc. Weigh it carefully and dissolve in 20 c.c. of a mixture of equal parts of nitric acid and water. For this purpose place the coin in a beaker, cover with a watch-crystal, and warm on the water-bath until it is entirely dissolved. Remove the watch-crystal after rinsing it with water and continue warming the solution until the nitrous fumes are entirely expelled. Transfer the solution to a 250-c.c. flask, rinsing the beaker thoroughly. Dilute the solution to the mark and shake thoroughly. Take out 50-c.c. portions with a pipette, dilute with 100 to 200 c.c. of water, add 5 c.c. of the ferric iron solution, and titrate with the sulphocyanate. Repeat the titration until duplicates are obtained. Calculate the per cent of silver in the coin.

PROBLEMS.

Problem 14. The combined weight of sodium and potassium chlorides was 2.5685 grams. 1.432 grams of chlorine was present. Calculate the percentage of potassium and sodium chloride present.

Problem 15. The combined weight of the sodium and potassium chlorides was 2.032 grams. When converted into sulphates, the weight was 2.385 grams. Calculate the percentage of sodium and potassium present.

CHAPTER XXVII.

DETERMINATION OF PHOSPHORIC ACID.

A GOOD many methods of determining phosphoric acid volumetrically have been devised. None of these methods give as reliable and accurate results as the gravimetric method. The great amount of labor necessary and the great length of time which must elapse from the beginning to the end of the gravimetric determination render the use of the volumetric methods very desirable. Three of the best of these methods will be described.

THE URANIUM METHOD.

This method is applicable to the titration of the phosphoric acid in the alkali and alkaline earth phosphates. IRON, and especially ALUMINIUM, if present in considerable amount, interfere seriously with the titration. The method is applicable to most of the material used for fertilizers, such as bones, bone-ash, soluble phosphates, phosphorite, etc. The method is based on the fact that when uranium nitrate or acetate is added to a neutral solution of a phosphate all of the phosphoric acid is thrown down as yellow uranyl phosphate, UO_2HPO_4 . Free mineral acid must be absent, but the solution may be moderately acid with acetic acid.

A very delicate INDICATOR for the excess of the uranium is found in the reaction with potassium ferrocyanide, which gives a decided brown tinge with very small amounts of uranium. Unfortunately, the method is not an absolute one, but gives results which vary with the volume of the solution, the salts present, etc., so that the standardization of the solution must be made under as nearly as possible the same conditions as the determination to be carried out. The standardization and determination should be

carried out by the same individual. To complete the precipitation of the phosphoric acid, the solution must be boiled after each addition of the standard solution. Some calcium phosphate is carried down with the uranium phosphate, so that if a solution containing calcium is to be titrated, the uranium solution must be standardized by calcium phosphate, as the alkali phosphates are not carried down in this manner. Several titrations must also be made, in the first adding the uranium solution in small amounts until the end-point is reached. In the second titration nearly all of the uranium solution is added at once.

518. Standard Solution.—The uranium solution is made by dissolving about 35 grams of uranium nitrate or acetate in water and diluting to a liter. $3\frac{1}{2}$ grams of ammonium or sodium acetate are added to the nitrate solution to neutralize any free acid present. The addition of 50 c.c. of pure glacial acetic acid to either the nitrate or the acetate solution renders it more stable on exposure to light. The nitrate may usually be obtained in a purer condition than the acetate, while the addition of an alkali acetate to the latter is unnecessary. The solution is allowed to stand for several days and is then filtered, or the clear liquid drawn off.

519. Standardization.—For standardizing the solution a pure salt or a solution of a phosphate in which the phosphoric acid has been accurately determined must be available. DISODIUM PHOSPHATE and MICROCOSMIC SALT may be recrystallized until absolutely pure, although some uncertainty always exists as to the amount of water present in the dried crystals. DIHYDRIC POTASSIUM PHOSPHATE has the advantage that it contains no water of crystallization. If these pure salts are not at hand, a solution may be made containing approximately 0.1 gram P_2O_5 in 50 c.c. 100-c.c. portions of this solution may be measured out and the phosphoric acid present determined by precipitation with magnesia mixture and weighing as magnesium pyrophosphate.

520. Titration.—50 c.c. of the standard phosphate solution is measured out into a beaker and heated to 90° or 100° . The uranium solution is added until a drop taken out and placed on a white porcelain surface gives a brown ring when the centre of the drop is touched with a glass rod which has been dipped in a freshly made solution of potassium ferrocyanide. This solution

is made by dissolving about $\frac{1}{4}$ gram of the salt in 20 c.c. of water. After each addition of uranium the solution is brought to a boil. The color of the spot test increases slowly on standing. The worker must therefore note the depth of color after a fixed interval of time. Uniformity in this respect is most readily secured by always observing the color after an additional drop has been added to the solution being titrated and the solution brought to a boil. When the end-point is reached, this drop will be in excess, but a correction may easily be made to the reading after noting the change in the reading of the burette produced by letting one drop fall from the burette. A second and third titration are made, adding nearly the entire amount of uranium solution at once. The uranium solution is then diluted so that 1 c.c. is equal to .005 gram of P_2O_5 .

521. Standardization with Calcium Phosphate.—When the uranium solution is to be used for the titration of phosphoric acid in the presence of calcium, it must be standardized by means of a solution of tricalcium phosphate. About 5.5 grams of the pure material is weighed out and dissolved in a little dilute nitric or hydrochloric acid. It is precipitated by adding a slight excess of ammonia and redissolved in a moderate excess of acetic acid. The solution is then diluted to a liter. The phosphoric acid in 50-c.c. portions of this solution is determined by precipitation as molybdate, dissolving in ammonia, and reprecipitating with magnesia mixture and weighing as magnesium pyrophosphate. The titration of 50-c.c. portions of this solution with the uranium solution is conducted as already given.

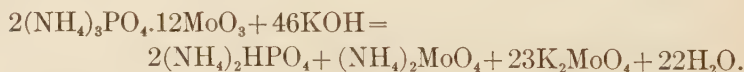
522. Titration of Phosphates.—The analysis of phosphates which are free from more than traces of iron and aluminium is made by dissolving weighed portions, so that 50 c.c. shall contain about 0.1 gram P_2O_5 . If the material is dissolved in the strong mineral acids, the solution must be neutralized with ammonia and then acidified with acetic acid. 50-c.c. portions are then titrated exactly as directed for the standardization.

When considerable iron or aluminium is present, the phosphoric acid must be separated from these elements by precipitation as phosphomolybdate, which is dissolved in ammonia, and the phosphoric acid again precipitated with magnesia mixture. The mag-

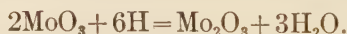
nesia precipitate is then dissolved in a little nitric or hydrochloric acid, the solution neutralized with ammonia and then acidified with acetic acid. The phosphoric acid is then titrated with the uranium solution.

TITRATION OF THE PHOSPHOMOLYBDATE.

Two volumetric methods of determining phosphoric acid have been based on the properties of the phosphomolybdate precipitate. By one of these methods, that of Pemberton,* the molybdic acid in this precipitate is titrated by means of standard caustic soda or potash with phenolphthalein as the indicator according to the following equation:



By the other method† the molybdic acid is reduced by means of zinc to molybdic oxide according to the equation:



The molybdic oxide is then oxidized by means of standard potassium permanganate solution.

523. Pemberton's Alkalimetric Method.—This method is applicable to the titration of the phosphates of the alkalis and the alkaline earths, but the results are not so good when considerable quantities of iron or aluminium are present. In the presence of large amounts of these metals, it is advisable to redissolve and reprecipitate the phosphomolybdate. As sulphuric acid may be carried down with the precipitate, it should be absent from the solution. If present it may be removed by means of barium chloride.

524. Standard Solutions.—A standard solution of nitric acid and one of caustic soda or potash free from carbon dioxide are required. The solutions are made of such a strength that 1 c.c. is equal to .001 gram of P_2O_5 . Since 46 molecules of caustic soda or potash are equal to 1 molecule of phosphorus pentoxide, a liter of

* Jour. Am. Chem. Soc., 1894, 278.

† Blair, The Chemical Analysis of Iron, 1901, p. 104.

normal solution will be equal to 1/46th of the molecular weight of P_2O_5 , or 3.087 grams. A solution of convenient strength will be .3239 normal, 1 liter of such a solution being equal to 1 gram of P_2O_5 . The nitric acid may be made by diluting 21 c.c. strong nitric acid (sp. gr. 1.40) to 1 liter. The caustic soda solution may be made by adding to 100 grams of pure caustic soda an amount of water just insufficient to dissolve it. After allowing the solution to settle in a tall covered vessel, 17 c.c. of the clear liquid is withdrawn with a pipette and diluted to 1 liter. Most of the sodium carbonate remains undissolved. If caustic potash is used, about 20 grams are weighed out and diluted to a liter. The carbon dioxide present must be precipitated by means of barium hydroxide or chloride. Both the caustic soda and caustic potash solutions must be protected from the carbon dioxide of the air.

525. Standardization.—The solutions may be standardized by any of the methods given in Chapters XXI and XXII. The acid must be compared with the alkali, using phenolphthalein as the indicator. A much better method of standardization consists in precipitating a known amount of phosphoric acid by means of the molybdate solution and titrating the precipitate in exactly the same manner as in the analysis of an unknown phosphate.

526. Precipitation of the Phosphoric Acid.—The molybdate solution is made according to the directions given on p. 507. For washing the precipitate, a dilute solution of nitric acid is used, a solution made by adding about 15 c.c. concentrated acid to 1 liter of water being suitable. The acid is washed out by means of a potassium nitrate solution made by dissolving 1 gram of potassium nitrate in 1 liter of water.

The phosphate must be free from organic matter. If present, it is destroyed by ignition of the material in a platinum dish or crucible. If the percentage of phosphoric acid is large, a solution should be made by dissolving a weighed amount in nitric acid and diluting to a known volume. Portions are then measured out containing not more than .050 gram P_2O_5 . The solution is nearly neutralized with ammonia, warmed to about 40°, and 40 c.c. of the molybdate solution added. The precipitation is best made in an Erlenmeyer flask of about 250 c.c. The solution is allowed to digest for ten to fifteen minutes, the temperature of about 40°

being maintained by warming on the water-bath. By closing the flask with a rubber stopper and shaking about five minutes, complete precipitation will be insured. Allow the precipitate to settle for a few minutes and decant the solution through a small filter-paper. Transfer the precipitate and wash with dilute nitric acid until free from molybdenum as indicated by the absence of a precipitate with ammonium sulphide. The precipitate is then washed with the potassium nitrate solution until free from acid. The washing must be thorough, but as little wash-water as possible must be used, because of the slight solubility of the precipitate. If properly done, 200 c.c. will be found sufficient.

527. Titration.—The paper and the precipitate are placed in a beaker and a measured amount of the standard caustic soda or potash solution sufficient to dissolve the precipitate is added. 10-c.c. portions may be added, and if on agitation the precipitate does not dissolve, another 10-c.c. portion is added. Continue the addition of 10-c.c. portions until the precipitate is completely dissolved. Add a few drops of phenolphthalein and titrate the excess of alkali with the standard nitric acid. The amount of phosphoric acid present is calculated from the number of cubic centimeters of caustic soda used.

REDUCTION OF THE MOLYBDATE PRECIPITATE WITH ZINC AND TITRATION WITH PERMANGANATE SOLUTION.

528. Standard Solution.—A standard solution of potassium permanganate will be required for this method. As 1 molecule of P_2O_5 is combined with 24 molecules of MoO_3 , which will require 36 atoms of oxygen to reoxidize after being reduced to Mo_2O_3 , we have the relation Mol. wt. $P_2O_5(142) = \text{Mol. wt. } 36 O(576)$. A liter of a normal solution of potassium permanganate will therefore be equal to 1.9722 gram of P_2O_5 . From this figure the value of a fifth- or tenth-normal solution may be computed. If standardized by means of iron, the value of the solution in phosphorus pentoxide may be calculated directly from the factor .03528, which is the equivalent of 1 gram of iron in phosphorus pentoxide. The best method consists in reducing and titrating the molybdate precipitate from a known amount of phosphoric acid.

529. Titration.—The precipitation of the phosphate with the molybdate solution is carried out exactly as given for the preceding method. Instead of washing with dilute nitric acid and potassium nitrate, a solution of acid ammonium sulphate is used. This is made by adding to 1 liter of water 15 c.c. of strong ammonia (sp. gr. 0.90) and 25 c.c. of concentrated sulphuric acid (sp. gr. 1.84). After washing the precipitate until it is free from the molybdenum solution, as indicated by the test with ammonium sulphide, it is dissolved in dilute ammonia. During the washing, the phosphomolybdate need not be entirely removed from the flask in which it was precipitated. The ammonia solution of the precipitate is allowed to flow into the flask together with the water used to wash the paper. 5 grams of pulverized zinc and 15 c.c. of concentrated sulphuric acid are now added. The flask is closed with a stopper through which passes a glass tube bent at a slightly acute angle and dipping into a saturated solution of sodium bicarbonate. When all of the zinc is dissolved the solution is titrated with the standard potassium permanganate solution. The solution before titration should be green in color. If it is brown the determination should be rejected. A blank should be made in which the same amount of ammonia, zinc, and sulphuric acid is added to enough distilled water to make the volume of the solution the same as that in the titration of the molybdate precipitate. After the zinc is dissolved, the solution is titrated with the standard permanganate and the amount added is subtracted from the volume used in the determination of phosphorus.

TECHNICAL ANALYSIS.

CHAPTER XXVIII.

ANALYSIS OF IRON AND STEEL.

IRON and steel as manufactured to-day are quite complex substances, containing almost invariably, besides IRON, the elements CARBON, SILICON, SULPHUR, PHOSPHORUS, and MANGANESE, while special varieties may contain NICKEL, CHROMIUM, MANGANESE, etc.

530. The Metals are undoubtedly present in the conditions in which they usually exist in alloys. The analysis for the determination of the amount of the metals present other than iron is carried out by the methods already given for the analysis of alloys.

531. The Acid Elements are for the most part combined directly with the iron as *carbide*, *silicide*, *sulphide*, and *phosphide*. As these elements are usually met with in combination with oxygen, the ordinary methods of analysis are not always suitable for their determination in iron and steel. The modification usually consists in adopting a method of dissolving the metal by which the acid element is certain to be thoroughly *oxidized*. Solution of iron or steel in a non-oxidizing acid like hydrochloric results in the evolution of more or less of the acid elements present as hydrogen compounds, such as *hydrogen sulphide*, *phosphine*, and various *hydrocarbons*. Silicon even is liable to be volatilized as *silicon tetrachloride*. When solution is effected with nitric acid, silicon, phosphorus, and sulphur are converted into non-volatile oxygen compounds, while more or less of the carbon is lost as carbon dioxide. For the determination of carbon, the iron is dissolved in solutions of cupric salts or the carbon dioxide evolved on dissolving the metal in an oxidizing solution is collected and determined.

The determination of these elements must be carried out with unusual care, since a very slight variation in the percentage

produces a very considerable variation in the properties of the metal.

532. To Obtain a Sample for Analysis a perfectly clean drill is taken, and by means of a drill-press or an ordinary brace, holes are bored in various parts of the casting or bar of iron or steel. Loose dirt, sand, etc., must be removed from the surface so as not to fall into the drillings. If the surface cannot be cleaned perfectly the first drillings should be discarded. The remainder of the drillings may then be collected on a piece of clean glazed paper. The iron may also be separated from sand and dirt by means of a magnet. Oil may be removed by washing a few times with ether. The drillings are usually fine enough for most purposes. If not, they may be crushed in an agate or hardened-steel mortar. In no case may the fine portions be taken and the large pieces discarded. A fair sample of both portions must be taken and further pulverized if necessary.

DETERMINATION OF SILICON.

533. Solution of the Iron in Nitric Acid.—One to five grams of the drillings are placed in a beaker of 200- to 300-c.c. capacity and 40 c.c. of a mixture of 20 c.c. concentrated nitric acid and 20 c.c. water are added. The action is generally quite violent accompanied by frothing, so that to prevent loss it should be moderated by placing the beaker in cold water. If action does not begin as soon as the acid is added, the beaker may be gently warmed and cooled when the action becomes violent. It may also be moderated by adding the acid in several portions. When the action has ceased, the beaker is warmed on the hot-plate to dissolve the few remaining portions of metal. Solution may be hastened by the addition of a little hydrochloric acid. The solution is evaporated to dryness and the residue heated in the air-bath until nitrous fumes are no longer evolved. The residue is then dissolved in 30 c.c. hydrochloric acid by warming gently. The solution is diluted somewhat, warmed, and the silica filtered off on an ashless paper and washed. Dilute hydrochloric acid is first used and then water.

534. Volatilization of Silica.—The moist paper is transferred to a weighed platinum crucible, the paper burned, and the precipi-

tate ignited, finally over the blast-lamp, and weighed. Even if the silica is perfectly white, it is necessary to test its purity by adding a few drops of concentrated sulphuric acid and then enough pure hydrofluoric acid to dissolve the silica. The solution is then evaporated to dryness and the residue ignited and weighed. The weight of the residue is subtracted from the weight of the impure silica and the amount of silicon calculated.

535. Drown's Method.—A more rapid method which is very much used for pig iron and which gives excellent results is based on the fact that the silicic acid may be dehydrated by heating with concentrated sulphuric acid. The drillings are dissolved in nitric acid as already described. 20 c.c. of sulphuric acid consisting of equal parts of concentrated acid and water are then added for each gram of drillings taken. The solution is heated until copious fumes of sulphuric acid are given off. The lumps of ferric sulphate must be broken up with a rod and the solution stirred to prevent bumping and spattering of the material. The concentrated acid is allowed to cool somewhat, cautiously diluted with water, and the solution warmed gently until the ferric sulphate is completely dissolved. The hot solution is filtered immediately, as the silica dehydrated in this manner gradually goes into solution again. The silica is washed first with water and then with dilute hydrochloric acid and finally with water. It is ignited and weighed, and then volatilized as directed in the first method. This method is used when silica alone is to be determined.

536. Solution of the Iron in Hydrochloric Acid.—The silica may also be determined after solution of the iron in hydrochloric acid and potassium chlorate. The evaporation of the solution to dryness may then be accomplished more rapidly, but a slight loss of silicon as SiCl_4 is almost inevitable.

537. Fusion of Silica Precipitate.—Instead of ascertaining the amount of impurity in the silica by treatment with hydrofluoric and sulphuric acids, it may be fused with four or five times its weight of sodium carbonate. The fused mass is dissolved in water, acidified with hydrochloric acid, evaporated to dryness, redissolved in hydrochloric acid and water, and the silica filtered off, washed, ignited, and weighed. The purification of the silica by volatiliza-

tion with hydrofluoric acid is more convenient if a pure acid is at hand.

DETERMINATION OF SULPHUR.

538. Solution of the Iron in Nitric Acid.—Sulphur may be determined in the filtrate from the silica by precipitation with barium chloride and weighing as barium sulphate. The iron must be dissolved by the first method given, but concentrated nitric acid must be used in place of the acid of sp. gr. 1.2 in order to insure complete oxidation of the sulphur. If the metal dissolves slowly, a few drops of hydrochloric acid may be added. As the percentage of sulphur is usually small, the large amount (5 grams) should be used. After solution has been effected a little sodium carbonate is added to prevent loss of sulphur trioxide, and the solution is evaporated to dryness. The residue is dissolved in hydrochloric acid, and again evaporated to dryness to completely remove the nitric acid and dehydrate the silicic acid. The residue is again dissolved in hydrochloric acid, and the excess expelled by evaporation. The solution must not be allowed to go to dryness, as a crust of insoluble basic ferric chloride would be produced. The solution is diluted and the silica and graphite filtered off and washed.

The filtrate is heated to boiling, and 10 c.c. of a 10% solution of barium chloride added slowly and with constant stirring. The solution is allowed to stand overnight in the cold. The precipitate is then filtered off and washed with very dilute hydrochloric acid until free from iron, and then with water. The barium sulphate is ignited and weighed in the usual manner.

539. Errors.—This method tends to give a low result on account of the solubility of barium sulphate in hydrochloric acid and ferric chloride. The result is apt to be high on account of the great difficulty of obtaining a precipitate of barium sulphate which is free from iron. The iron carried down seems to be present as a basic ferric sulphate which loses SO_3 on ignition and leaves the barium sulphate colored red by the ferric oxide. Fusing the precipitate with sodium carbonate, dissolving in water, and filtering effects a separation from the iron, but the barium sulphate obtained from the filtrate will not represent the sulphur present in the iron because

of loss of SO_3 during the first ignition. The presence of considerable amounts of hydrochloric acid in the iron solution tends to prevent the precipitation of the iron with the barium sulphate, but another error is introduced because of the marked solubility of the latter in the dilute hydrochloric acid and the ferric chloride. The large excess of barium chloride used tends to produce complete precipitation of the sulphuric acid. The success of the method therefore depends on regulating the amount of hydrochloric acid so as to prevent the precipitation of iron, but not that of the barium sulphate. The so-called *evolution methods* are therefore generally preferred when applicable. In steel the sulphur is generally so combined that the evolution method may be used, but the evolution of the sulphur is not complete in all pig and cast irons.

540. For Pig Irons the following method is used: After solution of the pig iron in strong nitric acid, 10 grams of sodium carbonate are added, and the solution transferred to a platinum dish, evaporated to dryness, and the residue ignited. It is then digested with water, a little sodium carbonate added, and the solution filtered. The insoluble material is washed with water containing sodium carbonate. The filtrate is acidified with hydrochloric acid and evaporated to dryness to dehydrate the silica, which is filtered off and washed. The sulphuric acid in the filtrate is precipitated with barium chloride and weighed as barium sulphate.

541. Determination of Sulphur in the Reagents.—All of the reagents used in sulphur determinations must be free from sulphur. Their purity is most easily assured by making a blank determination as follows: The total amount of nitric and hydrochloric acid used is measured out into a beaker, a little sodium carbonate added, and the solution evaporated to dryness. The residue is dissolved in a little water, a few drops of hydrochloric acid added, and after heating to boiling a few cubic centimeters of barium chloride solution are added. Any precipitate formed is filtered off, washed, ignited, and weighed, and the amount of barium sulphate obtained deducted from the amount obtained from the solution of iron.

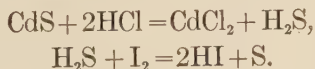
EVOLUTION METHODS FOR SULPHUR.

The evolution methods are now more largely used than the oxidation methods. In the evolution methods advantage is taken of the fact that when iron or steel is dissolved in hydrochloric acid the sulphur is evolved as hydrogen sulphide. Air as well as all oxidizing agents must be excluded from the evolution-flask.

542. For the Absorption of the Hydrogen Sulphide a large number of solutions have been suggested. Formerly a hydrochloric-acid solution of BROMINE was largely used. The sulphur was oxidized by this solution to sulphuric acid, which was precipitated and weighed as barium sulphate. The evolution of the disagreeable bromine fumes may be obviated by the substitution of an ammoniacal solution of hydrogen peroxide or a 3% solution of sodium peroxide. These reagents are, however, almost never free from sulphur, necessitating a separate determination of the amount present.

Another class of absorption liquids consists of solutions of metallic salts. The hydrogen sulphide is precipitated as a metallic sulphide, which in some cases is filtered off, washed, and weighed, and in other cases is oxidized by means of an appropriate solution to sulphuric acid which is precipitated as barium sulphate. The use of solutions of silver and copper for this purpose seems to be objectionable because of the reduction of the former by the hydrocarbons evolved, and the formation of an insoluble phosphorus compound in the latter. Alkaline solutions of lead, zinc, and cadmium seem to be very efficient absorbents. Very good results are obtained by washing the cadmium sulphide, drying at 100°, and weighing.

543. Iodometric Determination of the Sulphur.—The sulphur in the cadmium and zinc sulphides may also be determined by treatment with a measured excess of standard iodine solution, acidulating, and titrating the excess with standard sodium thio-sulphate. The following reactions then take place:



The hydrogen sulphide may also be absorbed by passing the gas directly through a measured amount of standard iodine solution and titrating the excess. The volatility of the iodine introduces an error in this determination. This may be obviated by absorbing the hydrogen sulphide in a solution of caustic soda and determining the sulphur with iodine solution in the same manner as with cadmium sulphide.

544. All of the Sulphur is not Evolved as Hydrogen Sulphide when a metal of high carbon content is analyzed. Organic sulphides are formed among which methyl sulphide $(\text{CH}_3)_2\text{S}$ has been identified.* These sulphur compounds are expelled from the evolution-flask with difficulty, and are not taken up so readily by the absorption solution. By passing the gases through a red-hot glass tube these compounds may be decomposed so that the sulphur is absorbed.

545. A Convenient Form of Apparatus for carrying out the determination is shown in Fig. 59. The Kipp generator is charged

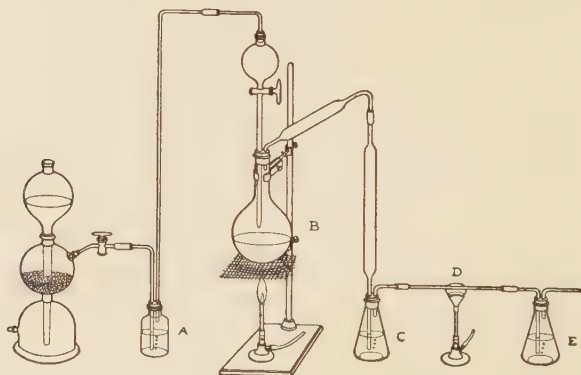


FIG. 59.

with zinc and acid for the generation of hydrogen. The wash-bottle A contains a solution suitable for the absorption of hydrogen sulphide.

A solution of LEAD NITRATE in CAUSTIC POTASH is very efficient. It is made by dissolving one part of caustic potash in two parts of water and pouring in a solution of lead nitrate with constant stirring until a permanent precipitate is produced. After being

* Philips, Stahl und Eisen, 16, 633.

allowed to settle, the clear liquid is siphoned off for use. It should be kept in a glass-stoppered bottle. The stopper should be coated with a little paraffine to prevent its sticking. This solution may also be used in the absorption-flasks *C* and *E*. 20 to 30 c.c. in each flask will be sufficient, water being added until the flasks are about half-full. The flask *B* should have a capacity of about $\frac{1}{2}$ liter.

546. Solution of the Iron.—Ten grams of filings are placed in the flask *B*. If a portion weighing 13.732 grams is used, the number of milligrams of barium sulphate obtained will be equal to the number of one-thousandths per cent of sulphur. If, for instance, .0156 gram of barium sulphate is obtained, the percentage of sulphur present will be .0156. The air in the apparatus is displaced with a stream of hydrogen. The glass tube *D* is then heated to redness, the dropping-funnel filled with dilute hydrochloric acid, and connection made immediately with the Kipp generator. About 20 c.c. of dilute acid should be used for each gram of iron. Some workers use for each gram of iron 19 c.c. of a dilute hydrochloric acid composed of equal volumes of concentrated acid and water, while others recommend 18 c.c. of a mixture of two-thirds dilute hydrochloric acid and one-third dilute sulphuric acid.

When the glass tube has been heated to dull redness the acid is allowed to flow into the flask *B* by turning the stop-cock of the dropping-funnel. The flask is heated with a Bunsen burner until the solution boils, a rapid stream of gas being allowed to pass through the apparatus. After boiling for about fifteen minutes the iron is usually dissolved.

547. Absorption of the Sulphur by Lead Solution.—The Bunsen burner is removed and the stream of hydrogen allowed to flow for about fifteen minutes more to sweep all of the hydrogen sulphide out of the apparatus. The precipitate in the flask *C* is filtered off on a small paper. If a precipitate has formed in the flask *D*, it is filtered off on the same paper and washed once or twice with hot water. The moist paper with the precipitate is thrown into a beaker, a little potassium chlorate added, and 5 to 20 c.c. of concentrated hydrochloric acid added, the amount used depending on the amount of lead sulphide present. Allow the beaker to stand in a warm place until chlorine is no longer evolved, dilute the strong

acid and filter. After washing the paper with hot water the filtrate is neutralized with ammonia and then acidified with 2 or 3 drops of hydrochloric acid. The sulphuric acid is then precipitated with barium chloride and weighed as barium sulphate.

548. Absorption of the Sulphur by a Cadmium Solution.—Instead of using an alkaline solution of lead nitrate in the absorption-flasks *C* and *D*, an alkaline solution of cadmium may be used as proposed by T. T. Morrel.*

The cadmium sulphide is filtered off on a Gooch crucible and washed with water containing a little ammonia. The precipitate is dried at 100° and weighed.

The cadmium sulphide together with the paper may also be placed in a beaker, 200 or 300 c.c. of cold water added, and then dilute hydrochloric acid until the precipitate is dissolved. A few cubic centimeters of freshly prepared starch solution are then introduced, and standard iodine solution added from a burette until a permanent blue color is produced.

DETERMINATION OF PHOSPHORUS.

The determination of phosphorus in iron or steel is invariably preceded by solution of the iron and oxidation of the phosphorus to phosphoric acid, which is then separated from the iron by precipitation as ammonium phospho-molybdate. The estimation of the amount of phosphoric acid may then be carried out gravimetrically or volumetrically by any of the methods given in Chapters IX and XXVII.

549. Oxidation with Nitric Acid and Separation of Silica.—From 1 to 5 grams of the iron or steel, according to the amount of phosphorus present, are dissolved in nitric acid, sp. gr. 1.2, about 15 c.c. being used for each gram of iron. Evaporate to dryness, and heat in the air-bath at 200° for one hour. At this temperature the oxidation of the phosphorus is completed. The residue is treated with 30 c.c. concentrated hydrochloric acid, and warmed until the oxide of iron is dissolved. The solution is evaporated to dryness again to dehydrate the silica. Dissolve once more in

* Chem. News. XXVIII. 229.

30 c.c. hydrochloric acid. Evaporate the solution to a sirupy consistency, dilute, and filter. The insoluble residue may be used for the determination of silicon, if that is desired.

550. Separation of Titanium.—If titanium is present it will form an insoluble phosphate which will remain with the silica and cannot be dissolved by means of hydrochloric acid. The paper containing the washed silica and graphite is transferred to a platinum crucible and burned. The silica is volatilized by treatment with hydrofluoric and a few drops of concentrated sulphuric acid and heating until the sulphuric acid is volatilized. The residue, consisting of TiO_2 and P_2O_5 , is fused for one half hour with 2 or 3 grams of sodium carbonate, the melt dissolved in water, and the solution containing the P_2O_5 as sodium phosphate is filtered. The filtrate from the insoluble sodium titanate is acidified with nitric acid and added to the first filtrate from the impure silica. The hydrochloric acid is then expelled by addition of 30 c.c. of concentrated nitric acid and evaporating nearly to dryness.

551. The Phosphoric Acid may be Precipitated, after nearly neutralizing the nitric acid with ammonia, by means of molybdate solution and determined gravimetrically as directed in Chapter IX, or volumetrically as directed in Chapter XXVII.

552. Oxidation with Potassium Permanganate.—The destruction of the organic matter as well as the complete oxidation of the phosphorus in the solution of the iron in nitric acid may be advantageously accomplished by means of potassium permanganate as well as by heating the dry nitrate at 200° . After dissolving the iron in nitric acid, 10 c.c. of a 1.5% solution of potassium permanganate is added and the solution boiled until the pink color is destroyed and the manganese is reduced to the dioxide. This precipitate is dissolved by the addition of small amounts of sulphurous acid, ferrous sulphate, or sodium thiosulphate. When the solution has cooled to about 40° , it is neutralized with ammonia, the precipitate dissolved with a little nitric acid, and the phosphoric acid precipitated by the addition of molybdate solution.

553. The Molybdate Precipitate may be directly weighed as directed in Chapter IX. It may also be titrated with standard caustic potash or soda as directed in Chapter XXVII, or with

standard potassium permanganate solution after reduction with zinc as directed in the same chapter.

DETERMINATION OF CARBON.

Carbon exists in iron and steel in several conditions, and the qualities of the metal are considerably influenced by the condition in which the carbon exists. Analytical methods are in use for determining the amount of carbon existing in two conditions. The so-called **FREE OR GRAPHITIC CARBON** as well as the total amount of carbon are determined directly. The **COMBINED CARBON** is usually determined by difference.

TOTAL CARBON.

a. SOLUTION OF IRON AND OXIDATION OF CARBON BY CHROMIC ACID.

This is a very accurate as well as a rapid and largely used method of determining carbon in all grades of iron and steel, with the exception of ferric chrome and irons high in silicon. The carbon is oxidized by the chromic acid to carbon dioxide, which may be absorbed in an appropriate apparatus and weighed or the volume of the gas may be measured and the weight calculated.

554. The Following Solutions are prepared for the combustion of the carbon.

1. Two hundred grams of copper sulphate are dissolved in a liter of water.

2. A saturated solution of chromic acid.

3. A solution made by taking 35 c.c. of solution 2, 190 c.c. of water, 750 c.c. of concentrated sulphuric acid, and 340 c.c. of phosphoric acid, sp. gr. 1.4.

After adding a few cubic centimeters of sulphuric acid, solution 2 should be heated to boiling to destroy any organic matter that might be present. Solution 3 should also be heated to boiling before use.

555. The Apparatus is set up as shown in Fig. 60. The round-bottomed flask *A* should have a capacity of about 250 c.c. The short piece of combustion tubing *B* is filled with lumps of copper oxide which are kept in place by short coils of copper gauze. The

tube is placed in a short tube furnace or is heated by several Bunsen burners. This tube is heated to redness during the combustion of the carbon in order to decompose the hydrocarbons evolved. If it is omitted, the result must be increased 2% for malleable iron and steel and $3\frac{1}{3}\%$ for pig iron. The presence of copper sulphate in the combustion-flask reduces the amount of the hydrocarbons evolved. The U-tube *C* is filled with calcium chloride for drying the carbon dioxide which is absorbed in the caustic potash bulb *D*. If this bulb is not fitted with a small calcium chloride tube, the U-tube *E* must be weighed as well as

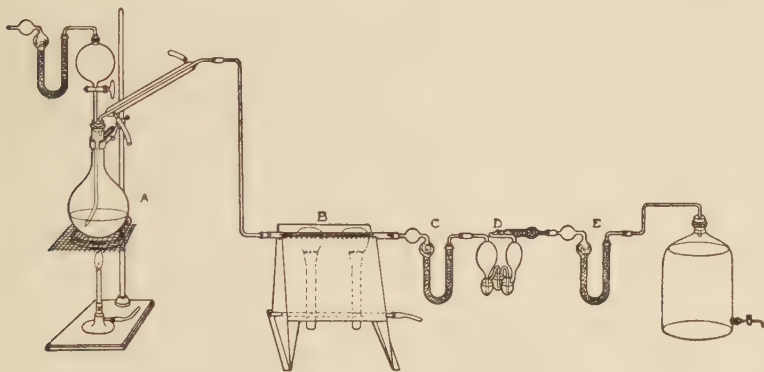


FIG. 60.

the caustic potash bulb *D*. Another calcium chloride tube must then be inserted between the U-tube *E* and the aspirator. The U-tube attached to the dropping-funnel is filled with soda-lime and serves to remove carbon dioxide from the air drawn through the apparatus. The apparatus is set up and tested for leaks as already directed for the determination of carbon dioxide in Chapters IX and XV.

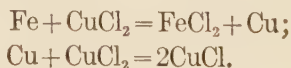
556. Process.—From 1 to 5 grams of the iron, depending on the amount of carbon present, is weighed out and placed in the flask *A*. 15 c.c. of copper sulphate solution is introduced through the dropping-funnel. After one or two minutes introduce 15 c.c. of the chromic acid solution and 135 c.c. of solution 3. Allow a slow stream of air to pass through the apparatus and heat the solution gently with the Bunsen burner, bringing it to a boil in fifteen to twenty minutes. Continue the boiling for about two hours.

Aspirate about 2 liters of air through the apparatus, disconnect the absorption-tubes, and weigh after allowing them to remain in the balance-case for about fifteen minutes.

b. WEIGHING OF CARBON AFTER SEPARATION OF THE IRON BY MEANS OF POTASSIUM CUPRIC CHLORIDE SOLUTION.

557. Action of Copper Solutions.—On treating iron or steel with a solution of copper, the copper is displaced by the iron which unites with the acid, forming a ferrous salt. The *combined carbon* as well as the *graphitic carbon remains undissolved*, no hydrogen or hydrocarbons being evolved.

Formerly a neutral solution of COPPER SULPHATE was employed. This has largely been replaced by a solution of CUPRIC AMMONIUM CHLORIDE, by which the iron is dissolved much more rapidly, the precipitated copper also going into solution. On account of the difficulty of obtaining the double ammonium salt free from organic material, the use of the double chloride of potassium and copper has arisen. It has also been recently shown by the American members of the International Steel Standards Committee that more accurate results are obtained by the use of a copper solution containing about 10 per cent of hydrochloric acid. The reactions taking place may be represented as follows:



The cuprous chloride produced in this manner may be **reconverted** into cupric chloride by passing chlorine through the solution until it smells strongly of chlorine. Blair* states that a solution regenerated in this manner is more active than a fresh solution. The same solution may be used repeatedly until the concentration of the iron salts is too great. Blair has used the same solution eleven times with good results.

558. The Solution of the Iron is effected by treating 1 gram of pig iron, spiegel, or ferromanganese with 100 c.c. of a saturated solution of the potassium cupric chloride and 7.5 c.c. of concentrated hydrochloric acid. 3 grams of steel or puddled iron are

* Chemical Analysis of Iron, 1901, p. 165.

taken and treated with 200 c.c. of the copper solution and 15 c.c. strong hydrochloric acid. The iron is dissolved very much more rapidly if the solution is stirred. After digestion for several minutes at the ordinary temperature the solution may be warmed gently, but not higher than 60° or 70°. If many determinations are to be made, a mechanical device for stirring should be used.

559. Direct Weighing of Carbon.—When the iron and the precipitated copper are completely dissolved* the carbon is filtered off and washed with hot water and a little hydrochloric acid to dissolve the copper and iron salts. If the iron or steel contains only combined carbon and is free from graphite the carbon may be weighed directly, after being filtered off on a Gooch crucible and dried at 100°. The carbon is then burned off and the residue weighed. The difference is carbonaceous matter which contains about 70% of carbon.

c. COMBUSTION OF SEPARATED CARBON IN A STREAM OF OXYGEN.

560. Filtration of Carbon on a Platinum Boat.—A more common and generally applicable method consists in burning the separated carbon in oxygen or chromic acid and collecting and weighing or measuring the carbon dioxide produced. If the carbon is to be burned in a stream of oxygen, the most suitable apparatus on which to filter it off and wash it is a platinum boat with perforated bottom which is of such a size that it may be placed in the glass or porcelain tube used for the combustion. A suitable holder is provided for the boat so that it may be used in the same manner as a Gooch crucible. Asbestos which has been ignited so as to free it from organic matter is made into a pulp by mixing with water, floated on the bottom of the boat and sucked into a smooth compact layer with the filter-pump. After filtering off the carbon on the boat and washing it, the whole is dried at 100° and transferred to the combustion-tube. Carbonaceous matter adhering to the sides of the beaker in which the iron was dissolved is wiped off with a wad of ignited asbestos held by a pair of forceps. The asbestos is then transferred to the boat.

* The metallic copper may easily be seen because of its bright-red color.

561. Filtration of Carbon on a Carbon Filter.—Instead of the perforated boat and holder a small platinum tube fitting into the combustion-tube may be used for filtering off the asbestos. The asbestos is held on a perforated platinum disk resting on a shoulder in the tube. After the carbon has been filtered off and washed, the disk is loosened by pushing it further into the tube by means of a glass or platinum rod. This is done to provide a passageway for the oxygen used in the combustion. After drying, the tube containing the asbestos and the carbon is inserted into the combustion-tube. An ordinary glass carbon filter may also be used in which the asbestos rests on a perforated platinum or porcelain disk or a spiral of platinum wire. After filtering off the carbon, the disk with the asbestos and the carbon is pushed out of the tube and transferred to a platinum boat. The particles of asbestos and carbon still adhering to the glass tube are wiped out by wads of ignited asbestos held in a pair of forceps. The boat and contents are then dried at 100° and transferred to the combustion-tube.

562. A Platinum, Glass, or Porcelain Combustion-tube may be used. It should be long enough to extend several centimeters beyond the furnace, so that the rubber stoppers are not softened by the heat. The forward half of the portion of the tube which is in the furnace is filled with granulated copper oxide which is held in place by short rolls of copper gauze. Another roll of copper gauze, to which a hook made of copper wire is fastened, is provided for insertion into the tube after the boat has been placed in the empty rear end.

563. A Stream of Oxygen is obtained from a steel tank which has been filled under pressure or from an ordinary gasometer which has been filled with oxygen by heating gently in a retort an intimate mixture of 1 part of powdered manganese dioxide and 20 parts of potassium chlorate. When the oxygen begins to be given off from this mixture the heating with the Bunsen burner must be discontinued or the evolution of gas will be too violent. The oxygen is purified by passing through a large U-tube or tower filled with soda-lime and pieces of fused caustic potash. A similar apparatus should be provided for purifying air.

564. Absorption Apparatus.—The carbon obtained from iron and steel is almost never free from sulphur. Some chlorides are

also generally present which cannot be washed out. Sulphur dioxide, hydrochloric acid, and chlorine are therefore given off on burning the carbon, and these gases must be absorbed before the carbon dioxide is allowed to pass into the caustic potash. A spiral of silver foil should be placed in the end of the combustion-tube for the absorption of the chlorine. A U-tube filled with pieces of pumice-stone which have been saturated with copper-sulphate solution and thoroughly dried at a little over 200° should be connected with the combustion-tube for the absorption of hydrochloric acid. For the absorption of sulphur dioxide a layer of lead peroxide is placed in the bottom of this tube and separated from the copper sulphate by means of wads of asbestos or cotton wool.

A U-tube filled with calcium chloride, a caustic potash bulb for the absorption of carbon dioxide, and a guard tube containing soda-lime and calcium chloride are attached in the order mentioned. After the apparatus has been tested for leaks in the usual manner, the combustion-tube is heated to redness and oxygen and air passed through to burn out any organic matter which may be present.

565. The Combustion.—The caustic potash bulb is weighed and replaced in the series of U-tubes. The boat containing the carbon is inserted in the combustion-tube and pushed in until it is close to the layer of copper oxide. The roll of copper gauze is inserted in the end of the combustion-tube, which is closed with the rubber stopper connecting with the supply of oxygen. The apparatus is tested for leaks by sucking out a little air so that the liquid rises in one limb of the caustic potash bulb. If this column of liquid remains at a constant height for at least five minutes the apparatus is tight. A slow stream of oxygen is now admitted, and two burners are lit under the forward end and one under the copper gauze in the rear end of the combustion-tube. When these portions of the tube are red-hot, the third burner from the forward end is lighted and then the other burners in order with a few minutes' interval. If a glass tube is used, the combustion may be observed by the glowing of the carbon. The combustion is usually complete fifteen minutes after the tube has become red-hot. The asbestos in the boat then appears nearly pure white.

The burners are then turned down and, after a few minutes, extinguished so as to cool the tube gradually. The stream of oxygen is replaced by a stream of air of which from 1 to 2 liters should be passed through the apparatus to sweep out the carbon dioxide. Neither the oxygen nor the air should pass faster than three bubbles per second. The absorption apparatus is then disconnected, wiped perfectly clean with a linen handkerchief, and after standing in the balance-case for not more than one-half hour is weighed. Until experience has been attained in conducting the combustion, it is advisable to insert the absorption apparatus and repeat the combustion to ascertain if any of the carbon remains unburned.

566. If Several Determinations are to be made a duplicate absorption apparatus should be prepared and weighed while the first combustion is in progress. When the first absorption apparatus is disconnected, the second is inserted, and a boat containing the carbon from another sample of iron is inserted in place of the first boat. During the progress of the second combustion the absorption apparatus of the first is weighed and may then be used for the third determination. When work is discontinued the entrance of air or other gases into the apparatus is prevented by closing all openings with glass plugs.

The carbon from which the iron has been separated may also be burned with chromic and sulphuric acids.

d. COMBUSTION OF THE SEPARATED CARBON WITH CHROMIC ACID.

567. An Apparatus similar to that shown in Fig. 61 is used. The flask *A* has a capacity of about 250 c.c. The U-tube *B* contains a sufficient amount of a solution of silver sulphate in concentrated sulphuric acid to fill the curved part of the tube. An empty U-tube *C* is placed next and then a U-tube *D* containing pumice-stone which has been saturated with copper sulphate solution and dried. The usual U-tube filled with calcium chloride for drying the carbon dioxide, the caustic potash bulbs, and the guard tube are then connected in the order mentioned.

568. The Combustion.—The asbestos containing the carbon is transferred to the flask and, after inserting the stopper, 10 c.c.

of a saturated solution of chromic acid is introduced through the funnel, followed by 100 c.c. of concentrated sulphuric acid which has been brought to the boiling-point after the addition of a little chromic acid. A slow current of air is passed through the apparatus and the flask is gently heated with the Bunsen burner and gradually brought nearly to the boiling-point. The heating is con-

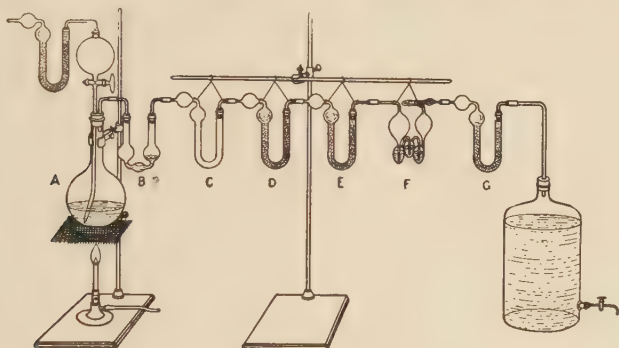


FIG. 61.

tinued until no more gas is evolved and the oxidation is complete. The current of air is continued until from 1 to 2 liters have passed through the apparatus, when the absorption-bulbs are disconnected and weighed.

e. DETERMINATION OF CARBON AFTER VOLATILIZATION OF THE IRON IN A STREAM OF CHLORINE.

The carbon in irons containing *chromium* and a large percentage of *silicon* can be determined only after volatilization of the iron in a stream of chlorine.

569. Separations Effected.—The iron is converted into ferric chloride, which can be completely expelled by heating the tube. The silica is also volatilized as silicon tetrachloride, SiCl_4 , and may be absorbed in water which will also contain any titanium present in the iron, being volatilized as titanium tetrachloride, TiCl_4 . These elements may be separated by adding to the solution concentrated sulphuric acid and evaporating to fumes. The silicic acid is dehydrated and may be filtered off and weighed while the titanium remains in solution. Any metals present

which form volatile chlorides will also be present in this solution. In the boat in which the iron was placed will remain all of the carbon, most of the manganese, chromic chloride, and the slag which was present in the iron.

570. Process.—The chlorine is generated in a large flask of about 1½ liters capacity, charged with 190 grams of manganese dioxide intimately mixed with 280 grams of sodium chloride. The chlorine is evolved on adding from a dropping-funnel 350 c.c. of a mixture of equal parts of concentrated sulphuric acid and water. The chlorine is washed by passing through water and dried by passing through concentrated sulphuric acid. The iron is spread over the bottom of a porcelain boat, which is placed in a glass combustion-tube which has been drawn out and bent at right angles where it emerges from the furnace so that it can dip under water. All connections must be made of glass as far as possible, the inner surface of rubber stoppers being coated with paraffine. The air is displaced from the apparatus by the stream of chlorine and the combustion-tube heated just sufficiently to expel the ferric chloride from the boat. This is usually accomplished by heating the tube to dull redness. The chlorides are dissolved out with water and the carbon filtered off on ignited asbestos, which is returned to the boat and dried. The carbon may then be burned in a combustion-tube in a stream of oxygen, or it may be burned with chromic and sulphuric acids as already directed.

DETERMINATION OF GRAPHITIC CARBON.

571. On dissolving iron and steel in acid, part of the carbon remains undissolved while part goes into solution or is evolved in combination with hydrogen. As graphite is insoluble in dilute acid, all of the carbon present in this form remains undissolved. If dilute hydrochloric acid is used a part also of the combined carbon remains undissolved. If nitric acid of specific gravity 1.2 is used, only the graphitic carbon remains undissolved. For this determination 1 gram of pig iron is taken, while as much as 10 grams of steel containing a very small per cent of graphitic carbon is taken. 15 c.c. of the nitric acid is taken for each gram of iron. The first violent action of the acid

is moderated by cooling the beaker with water. When all of the iron is dissolved, dilute the acid, filter off the carbon on ignited asbestos, and wash with water until free from iron. Treat the residue on the filter with a hot solution of potassium hydroxide of sp. gr. 1.1 to remove silica, and wash with water, then with dilute hydrochloric acid, and finally with water. Determine the amount of carbon present by burning in oxygen or in chromic acid as already directed.

DETERMINATION OF COMBINED CARBON.

The amount of combined carbon may be found indirectly by subtracting the amount of graphitic carbon from the total amount of carbon found.

572. Colorimetric Method of Eggertz.—This method is founded on the fact that when steel is dissolved in nitric acid of 1.2 specific gravity a brown color is given to the solution which is proportional to the amount of combined carbon present. Two specimens of steel which give the same depth of color contain the same percentage of combined carbon. If the colors differ, the darker solution may be diluted until the depth of color is identical. The ratio of the percentage of combined carbon in the two samples of steel will then be the same as the ratio of the volumes of the two solutions. If the percentage of combined carbon in one of the steels is known, the amount present in the other may be calculated. A so-called *standard steel* must therefore be selected and the percentage of combined carbon determined by one of the methods already given.

573. Standards.—It has been found, however, that two samples of steel containing exactly the same percentage of combined carbon give different colors if one sample has been treated differently, so far as tempering, hammering, etc., or if it has been made by a different process of manufacture. This peculiarity is believed to be due to the fact that the carbon exists combined in two different conditions, and when existing in one condition does not impart the same depth of color to the acid as when it exists in the other condition. Standards should therefore be at hand for each kind of steel to be tested, such as *Bessemer, crucible, open-hearth, etc.*,

and the rolling, hammering, tempering, etc., of the standard should as far as possible be the same as that of the sample to be analyzed. The percentage of carbon should also be as nearly as possible the same in the standard as in the steel to be analyzed.

574. Solution of the Steel.—A sufficient number of test-tubes 6 inches long and $\frac{5}{8}$ inch in diameter are taken and 2 grams of each sample, including the standard, are weighed out and placed in a test-tube. The test-tubes are carefully numbered to correspond to the numbers of the samples, and are placed in beakers or bottles containing cold water. Nitric acid of 1.2 specific gravity is then added to the test-tubes. Acid of this strength is made by diluting concentrated nitric acid (sp. gr. 1.4) with an equal volume of water. The acid is added from a burette, 3 c.c. being used for steels containing .3% of carbon; 4 c.c. for .3 to .5% of carbon; 5 c.c. for .5 to .8%; 6 c.c. for .8 to 1%; and 7 c.c. for over 1%. If the amount of carbon present is unknown, 3 c.c. of the acid should be added at first, and then successive portions of 1 c.c. as the increase in the depth of color or the presence of undissolved carbonaceous matter indicates the necessity for more acid. The nitric acid used must be absolutely free from chlorine. A small funnel or a glass bulb of suitable size should be placed in the mouth of each test-tube. The test-tubes are now immersed in the water of a water-bath while held upright by some suitable device, such as a metallic disk in which holes of the proper size to admit the tubes have been cut. The water is heated to boiling and the tubes shaken at intervals until the carbonaceous matter is completely dissolved, which will require from fifteen to forty-five minutes. As soon as solution is complete each tube is removed from the water-bath and placed in cold water, the light being excluded as much as possible. Direct sunlight bleaches the color very quickly.

575. For Comparing the Color of the Solutions Eggertz used graduated tubes. These tubes are of uniform bore, made of clear, colorless glass, and are carefully graduated from the bottom upwards, having a capacity of 30, or more, cubic centimeters. Transfer the solution having the lightest color to one of the tubes, using the same amount of water to rinse the test-tube as the volume of the solution. Mix the resulting solution thoroughly. In every case the acid solution of the steel must be diluted with at least as

much water as the amount of acid used to dissolve the steel in order to destroy the color due to the ferric nitrate.

The solution of the steel to be compared with the one first diluted is transferred to another tube in the same manner, and the color of the two solutions is compared by holding the tubes vertically and side by side in front of a piece of white paper between the observer and the light. The darker solution is diluted by the addition of water until the depth of color in the two tubes is identical. The percentage of combined carbon known to be present in the standard steel is divided by the volume of the solution of this steel. The quotient gives the amount of carbon represented by each cubic centimeter of the solution. This number multiplied by the number of cubic centimeters to which the solution of the steel to be analyzed was diluted gives the percentage of combined carbon present.

DETERMINATION OF MANGANESE.

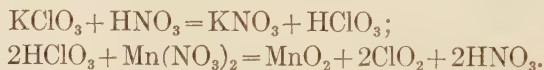
The difficulties attending the determination of manganese in iron and steel arise mainly from the presence of the large amounts of iron. The iron may be precipitated as basic acetate, but the precipitation must be repeated several times, and if the percentage of manganese is small, so that a large amount of iron must be taken for the analysis, the basic acetate precipitate becomes very large and unwieldy. The separation of the iron by solution of the ferric chloride in ether is a more rapid and convenient method, which has already been described in Chapter XIII, p. 160.

a. FORD'S METHOD.

Equally as efficient is a method known in this country as Ford's method.* Advantage is taken of the fact that potassium chlorate converts the manganese present in strong nitric acid solution into manganese dioxide, which can be filtered off from the iron which remains in solution. The separated manganese may

* Trans. Inst. Min. Engineers, IX, 397, X, 100.

then be determined gravimetrically or volumetrically. The reactions taking place may be represented as follows:



576. Solution of the Steel.—5 to 10 grams of steel or pig iron are taken, while only 1 gram of spiegel or ferro-manganese containing 20 to 40% of manganese, and $\frac{1}{2}$ gram if the per cent of manganese is still higher. If less than 0.2% of silicon is present, the weighed portion is dissolved in 60 c.c. of nitric acid of 1.2 specific gravity and the solution evaporated to small bulk. A large beaker should be used and the acid added cautiously. If the percentage of silicon is high, the steel should be dissolved in hydrochloric acid and the solution evaporated to dryness to dehydrate the silica, which otherwise forms a gelatinous mass and interferes with the subsequent filtration. Pig iron is also dissolved in hydrochloric acid, the solution filtered, and the filtrate evaporated to dryness. The hydrochloric acid is removed in either case by evaporation with 50 c.c. of strong nitric acid to a small bulk. The silica may also be removed by dissolving the iron in nitric acid to which a few drops of hydrofluoric acid have been added and evaporating to a small bulk.

577. Precipitation of the Manganese.—This solution, as well as that obtained from the steel low in silica, is treated with 100 c.c. of concentrated nitric acid and 5 grams of potassium chlorate added. The solution is boiled for fifteen minutes, 50 c.c. strong nitric acid are added, and 5 grams of potassium chlorate, and the solution again boiled for fifteen minutes. When no more chlorine fumes are evolved the solution is rapidly cooled by standing the beaker in cold water and the precipitate filtered off on asbestos. It is washed with strong nitric acid and then with water. It is advisable to keep the strong nitric acid filtrate separate from the wash-water and to test it for manganese by adding a little more potassium chlorate and again boiling.

578. If the Manganese is to be Determined Gravimetrically the manganese dioxide is dissolved in sulphurous acid or hydrogen peroxide and hydrochloric acid. The excess of the sulphur dioxide

or hydrogen peroxide is expelled by boiling the solution. The small amount of iron present is oxidized by the addition of a little bromine water the excess of which must be boiled out. It is precipitated by adding an excess of ammonia to the hot solution. The precipitate is filtered off, washed once or twice, dissolved in hydrochloric acid, and the solution boiled to expel a trace of chlorine from the manganese dioxide and reprecipitated with ammonia, filtered off, and washed thoroughly. The combined filtrates contain all of the manganese and a little cobalt if that element was present in the iron. The cobalt may be precipitated by passing hydrogen sulphide through the solution after acidifying with acetic acid and heating to boiling. After filtering off the precipitate and boiling the solution to expel the excess of hydrogen sulphide, the manganese may be determined either as sulphide or as phosphate as directed in Chapters VI and VII.

579. The Manganese may also be Determined Volumetrically by dissolving the manganese dioxide in excess of oxalic acid or a pure ferrous salt and titrating the excess with a standard solution of potassium permanganate (see pp. 322, 325). As the per cent of oxygen in the precipitate may not be exactly that corresponding to the formula MnO_2 , it is advisable to standardize the potassium permanganate solution by using the precipitate obtained from a sample of steel or iron in which the manganese has been determined gravimetrically. The manganese dioxide obtained from a weighed amount of this iron is dissolved in excess of a reducing agent and the excess determined by means of the permanganate solution.

b. VOLHARD'S METHOD.

580. Solution of the Metal.—This very accurate method of determining manganese may be used for determining this element in all samples of iron and steel except those containing very minute amounts of manganese. Weigh out 5 grams of ferromanganese and from 1 to 2.5 grams of spiegeleisen, white pig iron, steel, etc. Dissolve* in a mixture of 275 c.c. of water 125 c.c. of

* Reis, Zeit. f. angew. Ch., 1892, pp. 604, 672.

concentrated nitric acid (sp. gr. 1.4) and 100 c.c. concentrated sulphuric acid. Use from 25 to 50 c.c. of this acid mixture, according to the amount of iron taken. After the iron is dissolved, evaporate the solution until fumes of sulphuric acid are evolved. After cooling, add 100 c.c. of water and 10 c.c. of the acid mixture and warm until solution is complete. Transfer to a flask of 750- to 1000-c.c. capacity and add 3 grams of barium peroxide and 5 c.c. concentrated nitric acid to oxidize the hydrocarbons present. Boil several minutes to decompose the excess of barium peroxide.

581. Titration.—Dilute the solution until the flask is about one-half full, add zinc oxide suspended in water, shaking the solution after each addition until the solution is neutral and the iron is precipitated, leaving it colorless or slightly milky with the excess of zinc oxide. Warm the solution to about 90°, but not to boiling, and titrate with standard potassium permanganate solution as directed in Chapter XXIV, page 323.

582. If the Zinc Oxide contains manganese it may be purified as follows: Dissolve the impure oxide in hydrochloric acid, finally adding an excess of the zinc oxide so that part of it remains undissolved. Add a little bromine and heat the solution to boiling and filter. Precipitate the zinc oxide by means of ammonia, carefully avoiding an excess. Wash the oxide thoroughly and then transfer to a bottle with water. Shake the bottle well before withdrawing any of the oxide for use.

*c. DESHAY'S METHOD.**

This method is based on the fact that manganese nitrate when boiled with nitric acid and lead peroxide is converted into permanganic acid, which may then be titrated with a standard solution of sodium arsenite. The method is especially applicable to iron and steel containing less than 2% of manganese. It cannot be used when chromium is present, as chromic acid is produced.

583. Process.—0.5 gram of steel or pig iron is dissolved in a small beaker or test-tube in 30 c.c. nitric acid of 1.2 specific gravity. The solution is boiled until the nitrous fumes are completely

* Bull. Soc. Chim. de Paris, June 20, 1878.

expelled. From 1 to 3 grams of lead peroxide or red lead free from manganese are then added and the solution diluted with hot water to about 60 c.c. It is boiled for three or four minutes and after allowing the peroxide of lead to settle, the solution is decanted and the residue again boiled after the addition of 50 c.c. of dilute nitric acid. If the solution again becomes colored with permanganic acid, it must be decanted and the boiling repeated after the addition of dilute nitric acid. The solution is filtered through asbestos which is free from organic matter. The filtrate is titrated with a standard solution of sodium arsenite.

584. The Sodium Arsenite Solution may be made by dissolving 4.5 grams of pure arsenious oxide in water to which 25 grams of sodium carbonate has been added and diluting the solution to 2 liters. This solution should then be standardized by comparison with a standard potassium permanganate solution, or a still better plan is to standardize it with a sample of steel in which the manganese has been determined gravimetrically. This is done by weighing out $\frac{1}{2}$ gram of the steel, dissolving in nitric acid, and oxidizing with peroxide of lead. The permanganic acid produced in this manner is titrated with the arsenite solution to be standardized. The amount of manganese corresponding to 1 c.c. of the arsenite solution may then be calculated from the known amount of manganese in the steel used.

585. Separation of Lead Peroxide by a Centrifugal Machine.—Instead of filtering the permanganic acid from the lead peroxide, the separation may be effected by means of a centrifugal machine. In order to secure complete oxidation of the manganese by boiling once, a smaller amount of the steel is taken, from .05 to .10 gram being used. 10 c.c. of the nitric acid of sp. gr. 1.2 are added to dissolve the iron and after the nitrous fumes have been expelled by boiling, 10 c.c. of hot water and $\frac{1}{2}$ gram of lead peroxide are added and the solution boiled for three minutes. The solution is washed into a wide-mouthed two-ounce bottle, enough water being used to make 50 c.c. The bottle is then placed in the centrifugal machine and rotated for two minutes. The liquid will then be perfectly clear and may be poured out without disturbing the lead peroxide, which forms a compact layer on the bottom of the bottle. The permanganic acid is then titrated with a solution

of sodium arsenite which is equal to about .0001 gram of manganese per cubic centimeter.

PROXIMATE ANALYSIS OF COAL.

The methods used in the analysis of coal do not give the amount of any definite chemical compound which is present in the coal. The determination of **MOISTURE** gives very nearly the amount of water present, but as this constituent is obtained by loss in weight after drying the coal in the air, an error is introduced because **SULPHUR** and other constituents present are oxidized at the temperature used for drying the coal, and therefore the coal loses weight for a time, and then begins to increase in weight. The conditions under which this as well as other determinations are made are somewhat arbitrarily fixed so that the results obtained by various chemists may be comparable with each other and form a basis for the comparison of the coals analyzed. The methods given in this chapter are those adopted by a committee of the American Chemical Society, consisting of Wm. A. Noyes, W. F. Hillebrand, and C. B. Dudley.*

586. The Determination of Moisture is made by heating 1 gram for one hour at 104° to 107° . This temperature may most readily be maintained by using a double-walled air-bath in which pure toluene is boiled. By attaching a reflux condenser to the usual steam vent, loss of toluene may be obviated. As considerable moisture is lost in powdering the coal, the committee recommends the making of two determinations of moisture, one on the coal as powdered for the determination of sulphur, ash, etc., and another on the material broken up only sufficiently fine for sampling. As it is necessary that the percentages found shall apply to the unpowdered coal as it is actually used, a correction must be made on the percentages found by using the powdered material. The difference in the percentages of moisture found is divided by the sum of the percentages of the other constituents in the powdered coal. The quotient multiplied by 100 is the percentage by which

* Jour. Am. Chem. Soc., XXI, 1116.

the percentages of the other constituents are reduced. The illustration given in the report mentioned is as follows:

	Coarsely Ground Coal.	Powdered Coal.
Moisture.	12.07	10.39
Volatile combustible matter.		34.25

The correction factor will be

$$\frac{12.07 - 10.39}{100 - 10.39} = \frac{1.68}{89.61} = .0187.$$

The true per cent of volatile combustible matter will be

$$34.25 - (34.25 \times .0187) = 33.61.$$

587. The Volatile Combustible Matter is determined by heating a fresh portion of the powdered coal in a tightly closed platinum crucible with the full flame of a Bunsen burner for seven minutes. The loss in weight less the moisture is the volatile combustible matter, while the residue in the crucible is the coke.

This determination serves to distinguish the different kinds of coal which are mined for various industrial purposes. The **ANTHRACITE COALS** give only a small per cent of volatile combustible matter, leaving a residue in the crucible which can hardly be distinguished from the powdered coal. The **BITUMINOUS** and **CANNEL COALS** melt on being heated in the crucible, and the volatile matter in escaping produces a porous mass which is much more bulky than the original coal. This material is what is known in commerce as "**COKE**." A good bituminous coal gives about 60% of coke. Cannel coals, on the other hand, give 60% or 70% of volatile combustible matter with a corresponding smaller per cent of coke. Between these extremes coals may be found, giving nearly all percentages of coke and volatile combustible matter.

588. The Percentage of Ash is found by burning a weighed portion of the coal in a platinum crucible. The percentage of ash subtracted from the percentage of coke gives the percentage of **FIXED CARBON**, the volatile combustible matter being composed of carbon which has united with the hydrogen present, forming volatile combustible hydrocarbons.

It is evident that a low percentage of ash in coal is very desirable, as this constituent not only has no calorific value, but forms a waste product which must be disposed of.

589. For Determining Sulphur various methods have been proposed and used, the difference being found in the methods of oxidizing the carbon and the sulphur, which are ultimately precipitated by means of barium chloride and weighed as barium sulphate. **ESCHKA'S METHOD**, by which the coal is burned by the oxygen of the air after mixing with magnesium oxide and sodium carbonate, and the sulphur oxidized by means of bromine water, is one of the most rapid as well as a very accurate method. As the sulphuric acid is extracted from the alkaline flux with hot water, some of the silica in the coal is also dissolved, and this is subsequently carried down with the barium sulphate. More accurate results may be obtained by evaporating the solution to dryness after acidifying with hydrochloric acid in order to dehydrate and remove this silica.

590. The Sulphur Exists in Coal in at least three conditions: as a **METALLIC SULPHIDE**, especially **PYRITES**, as **CALCIUM OR BARIUM SULPHATE**, and as a **SULPHURETTED HYDROCARBON**. In a proximate analysis of coal about one-half of the sulphur existing as pyrites and all of the organic sulphur is probably volatilized with the volatile combustible matter. The remainder of the sulphur existing as pyrites is expelled during the combustion of the fixed carbon, only that existing as barium or calcium sulphate remaining with the ash unless calcium or barium carbonate was present in the coal.

EXERCISE 70.

Proximate Analysis of Coal.

The carefully selected sample is coarsely ground in a porcelain mortar and well mixed. A few grams are taken and powdered and placed in a well-stoppered bottle. The main portion of the sample is preserved in the same manner.

591. Determination of Moisture.—The temperature of an air-bath is brought to 104° – 107° by adjusting the flame of the Bunsen burner. Two platinum or porcelain crucibles are cleaned and, after drying for a few minutes in the air-bath, are cooled in desiccators and weighed. One gram

of the coarsely ground coal is weighed and placed in one of the crucibles, while one gram of the powdered material is weighed out and placed in the other. The uncovered crucibles are then placed in the air-bath and heated for one hour. They are then cooled in the desiccators after replacing the covers, and weighed. If porcelain crucibles have been used, the coal is carefully brushed out and the crucibles weighed, as the latter may have lost weight during the heating. The loss in weight in each case in centigrams gives the percentage of moisture. The percentage found in the coarsely ground material is reported, while the difference between this percentage and that found in the powdered material is used to calculate the correction on the percentage of the other constituents.

592. Determination of Volatile Combustible Matter.—A 20- to 30-gram platinum crucible is cleaned, placed on a platinum or pipe-stem triangle, and ignited with the Bunsen burner. It is cooled in a desiccator and weighed. One gram of the powdered coal is weighed out and transferred to the crucible, which is placed on a large ring of the iron ring-stand, and the height of the ring so adjusted that the bottom of the crucible is 6 to 8 cm. above the top of the Bunsen burner, which must have a clear blue flame fully 20 cm. high when burning free. The cover of the crucible, which must fit tight, is adjusted, and the lighted burner placed under the crucible, which is heated seven minutes. The crucible must be protected from draughts during the heating, and the upper surface of the cover must burn clear. The hot crucible is transferred to the desiccator, and after cooling for fifteen to twenty minutes is weighed. The loss in weight less the moisture in the powdered coal is the volatile combustible matter. Compute the percentage, making the correction for difference in percentage of moisture in the coarsely ground and powdered coal.

COKE.—The residue in the crucible is COKE. The percentage is corrected as already directed.

593. Ash is determined by burning one gram of the coal placed in a platinum crucible. The portion used for the determination of moisture may be taken, or a fresh portion of the powdered material may be weighed out. The coke left after expelling the volatile matter burns with difficulty. The crucible is placed on its side on a pipe-stem or platinum triangle, and is heated at first with a very low flame. The burner must not be placed so that the flame passes in front of the crucible, thus preventing access of air. The combustion is accelerated by bringing fresh portions of coal to the surface by turning the crucible when the carbon has burned out, leaving the nearly white ash on the surface. When no more black particles are visible which burn on exposure to the air, the crucible is cooled in the desiccator and weighed, and the percent of ash calculated. The per cent of coke minus the per cent of ash gives the per cent of FIXED CARBON.

594. Determination of Sulphur by Eschka's Method.—An intimate mixture of 1 part of dry sodium carbonate and 2 parts of magnesium oxide is made. The magnesium oxide must be light and porous, not compact and

heavy. One and one-half grams of this mixture are weighed and placed in a large platinum crucible, or, still better, in a platinum dish having a capacity of 75 to 100 c.c. One gram of the finely powdered coal is weighed out and placed on the magnesia mixture, and the two thoroughly mixed by stirring with a platinum or glass rod. The dish is heated very cautiously with the Bunsen burner, which is at first held in the hand. The heat is raised very slowly, especially with soft coals. When the strong glowing has ceased the heat is gradually increased, until in fifteen minutes the bottom of the dish is at a low red heat.

When the carbon is completely burned the residue is transferred to a beaker, the dish is rinsed with about 50 c.c. of water, 45 c.c. of bromine-water is added, and the solution is boiled for five minutes. After allowing the insoluble matter to settle the solution is decanted through a filter. The residue is treated twice with 30 c.c. of water, which is brought to a boil, and decanted through the filter, which is then washed until the filtrate gives only a slight opalescence with silver nitrate and nitric acid. To the filtrate, which should have a volume of about 200 c.c., $1\frac{1}{2}$ c.c. of concentrated hydrochloric acid or 3 c.c. of dilute acid are added. The solution is boiled until the bromine is expelled, and 10 c.c. of a 10 per cent solution of barium chloride is added drop by drop with constant stirring, especially at first. Digest on the hot plate until the solution is clear, filter off the barium sulphate, and wash free from chlorides with hot water. Transfer the moist precipitate to a weighed platinum crucible which is heated with a small flame until the paper is burned. Finally heat to redness, cool in the desiccator, and weigh.

A BLANK DETERMINATION should be made to ascertain if the fusion mixture is free from sulphur. This determination is carried out exactly as directed for the determination of sulphur in the coal. The amount of barium sulphate obtained is subtracted from that obtained from the coal. The percentage of sulphur is then calculated.

If the coal contains much pyrite or calcium sulphate, the residue of magnesium oxide must be dissolved in hydrochloric acid and barium chloride added to the hot solution. Any barium sulphate precipitated is filtered and weighed as already directed.

595. Determination of Sulphur with the Parr Calorimeter.—If a determination of the calorific value of the coal is made by means of the Parr calorimeter, the sulphur may be conveniently determined in the same sample. The sodium peroxide oxidizes the sulphur to sodium sulphate. The cartridge is placed in a porcelain dish and the fused mass dissolved out with hot water. After rinsing the cartridge thoroughly, the solution is acidified with hydrochloric acid and evaporated to dryness on the water-bath to dehydrate the silica. The residue is taken up with water and a little hydrochloric acid, and filtered. After washing the paper free from chlorides, the solution is heated to boiling and the sulphuric acid precipitated by means of barium chloride, which is added slowly and with constant stirring. The precipitate is filtered off on a quantitative paper, washed free from chlorides, and ignited and weighed in the usual manner.

DETERMINATION OF THE CALORIFIC VALUE
OF FUELS.

596. Effect of Composition on Calorific Value.—The results of a proximate analysis of a fuel give only a general idea of its calorific or heating value by indicating the class in which the fuel belongs. Anthracite coals are characterized by a small percentage of volatile combustible matter (usually less than 10%), while bituminous coals contain a large amount of this constituent (usually 30–40%), and in cannel coals this is the main constituent. The proportion of this constituent is dependent on the amount of hydrogen present, as this element forms volatile compounds with the carbon. When hydrogen burns, it evolves a much larger amount of heat than is produced by the combustion of the same amount of carbon. Coals containing a large proportion of volatile combustible matter have therefore generally a high calorific value. On the other hand the calorific value is reduced by the presence of ash which has no calorific value, and by water which absorbs heat when it is converted into steam. It is evident that the calorific value of a fuel could be calculated from the percentage of carbon and hydrogen present. This method is subject to the error arising from the fact that the heat of combustion of hydrogen and carbon varies with the nature of their chemical combination with each other. Direct methods for determining calorific values are therefore more reliable. The instruments devised for this purpose are called calorimeters.

597. Thermal Units.—Various units for measuring heat are in use. They are all based upon the fact that a definite amount of heat will raise the temperature of a definite amount of water a definite number of degrees. Those based on the metric system are the large and the small calorie. A small calorie is defined as the amount of heat necessary to raise 1 gram of water from 4° to 5° Centigrade. The large calorie is the amount of heat necessary to raise 1 kilogram of water from 4° to 5° C., and is equal to 1000 small calories, and is denoted by the capital C. A unit of heat equal to 100 small calories has also been used, and is designated by K.

As the specific heat* of water changes but slightly with ordinary changes of temperature, only a very slight error will be introduced by using other temperatures than 4° to 5° C. when measuring the rise in temperature. For practical purposes, therefore, a calorie may be defined as the heat necessary to raise one gram of water one degree Centigrade. Another unit of heat in common use is the British Thermal Unit, designated by the initial letters B. T. U. This unit is the amount of heat necessary to raise the temperature of 1 pound of water from 39° to 40° Fahrenheit, or, for ordinary purposes, one degree F. at ordinary temperatures.

The heat of combustion of a fuel may therefore be expressed in calories or in B. T. U., the relation between these units being easily calculated from the known equivalents of grams and pounds and degrees Centigrade and degrees Fahrenheit (large calorie = 3.96832 B. T. U.). However, when the heat of combustion of a substance is given in calories, 1 gram or 1 kilogram is the amount of the substance for which the heat is given, while if the heat is given in B. T. U., the number given refers to the amount of heat obtained from 1 pound of combustible substance. As 1 kilogram = 2,20462 pounds,† to convert the heat of combustion in calories to the heat of combustion in B. T. U., multiply the number of calories by 1.8 ($3.96732 \div 2.20462$).

598. Calorimeters embody three essential features: (a) A combustion chamber; (b) a tank of water with a delicate thermometer for indicating the amount of heat absorbed; and (c) an insulating device to prevent the external heat from reaching the water and the thermometer, and also to prevent the heat generated in the combustion chamber from escaping from the apparatus.

599. The Bomb Calorimeter of Berthelot is the most accurate calorimeter which has been devised. It is adapted for the combustion of any solid or liquid combustible substance. The bomb is the

* SPECIFIC HEAT OF WATER ACCORDING TO ROWLAND AND PERUET.

° C.	° C.	° C.	° C.	° C.
5 1.0054	9 1.0026	13 1.0009	17 0.9993	21 0.9977
6 1.0047	10 1.0019	14 1.0005	18 0.9988	22 0.9974
7 1.0040	11 1.0014	15 1.0000	19 0.9984	23 0.9974
8 1.0033	12 1.0012	16 0.9995	20 0.9979	24 0.9972

† For these and other equivalents see Van Nostrand's Chemical Annual.

characteristic part of this instrument. It consists of a brass or steel receptacle of 400 to 600 cubic centimeters capacity, which can be tightly closed and can sustain a pressure of at least 25 atmospheres. A small platinum cup is suspended from the lid of the bomb. The substance to be burned is placed in this cup. Two insulated wires are led through the lid and extend to within a short distance of the cup. These wires are connected with a short piece of fine iron or platinum wire which can be fused by means of an electric current and thus ignite the combustible material at any desired moment. Pure oxygen under pressure is led into the bomb by means of a tube passing through the lid and containing a close-fitting valve. The oxygen is forced in until a pressure of 25 atmospheres is produced. In this atmosphere of pure oxygen under pressure, all substances may be burned.

The bomb is immersed in a tank of water in which a delicate thermometer is suspended to register the increase in temperature, the water being agitated by means of an appropriate stirring device to insure uniform distribution of the heat. The tank of water is enclosed in a vessel made of some good insulating material.

THE PARR CALORIMETER.

600. Chemical Reactions Involved.—This instrument differs from the bomb calorimeter in that sodium peroxide or other strong oxidizing substances are mixed with the fuel to produce the combustion. This results in two decided advantages. In the first place the combustion chamber may be very materially reduced in size (from 300 to 600 c.c. in the bomb calorimeter to 25 c.c. in the Parr calorimeter). In the second place the combustion chamber is not required to stand high pressure because the oxygen is not present as a gas under pressure and the products of combustion (CO_2 , SO_3 , H_2O , etc.) are not given off in the gaseous form. The alkali resulting from the decomposition of the sodium peroxide combines with the carbon dioxide, sulphur trioxide, and water, forming sodium carbonate, sodium sulphate, and sodium hydroxide. Very little gas pressure is therefore produced in the combustion chamber. An additional error is introduced, however, because heat is evolved by the combination of the products of combustion with the alkali.

These are mainly carbon dioxide and water. The former reacts with the sodium oxide to form sodium carbonate, while the latter forms sodium hydroxide. The chemical reactions which take place may therefore be represented in simple form by the following equations:

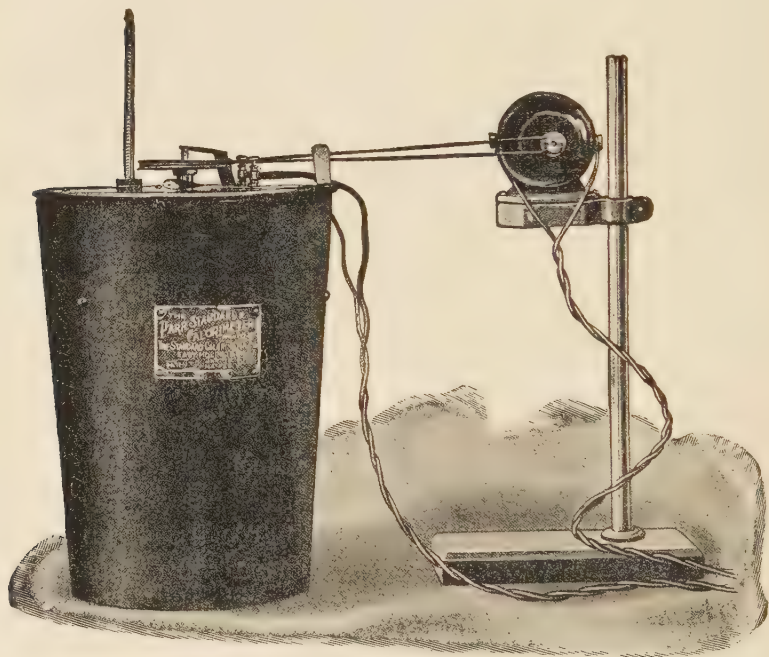


FIG. 62.

It has been found by experience as well as by calculation from the heats of formation of the compounds given in the equations, that very nearly 73 per cent of the heat produced in the reaction is due to the oxidation of the carbon to carbon dioxide and of the hydrogen to water. The factor 0.73 is, therefore, used as a correction constant in the final calculation.

601. The Sodium Peroxide.—Another source of error is met with in the fact that sodium peroxide readily absorbs water, forming the compound $\text{Na}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$. When heated this compound decomposes

into sodium hydroxide, oxygen, and water, with evolution of heat. In one experiment 10 grams of sodium peroxide absorbed 0.5 gram of water during an exposure of 1 hour to the air. The presence of this amount of water caused an increase of 0.194 degree during the combustion.

A special grade of sodium peroxide is, therefore, manufactured for the Parr calorimeter. It is carefully protected from exposure to the air and is sold in hermetically sealed tin cans. When desired for use, the contents of the can are transferred to a glass jar provided with a tightly fitting lid. Glass-stoppered bottles are not satisfactory. The "Lightening" or "Putnam" jar, which closes with a lever clamp, has been found well adapted for this purpose. The sodium peroxide must also be finely divided. It is not advisable to attempt to grind ordinary samples of the peroxide because of the unavoidable exposure to the air.

602. Construction of the Instrument.—Fig. 63 shows the construction of the cartridge which is made of brass. Both top and bottom are held in place by means of the cylinders or caps *F* and *E* which are screwed to the body of the cartridge. The joints are made air-tight by means of rubber washers. An insulated wire *J* passes down through the stem and at *I* is connected to the wire *H* by means of a piece of soft iron wire which may be fused by means of an electric current and thus ignite the combustible mixture in the bottom of the cylinder.

Fig. 64 shows the cartridge *D* in place in the instrument. It rests on a pivot at *F* and can be rotated by means of the pulley *P*. The blades attached to the center of the cartridge tend to force the water downwards within the cylinder *E*, and produce an upward current outside of this cylinder, thus keeping the temperature of the water uniform. Both the small cylinder *E* and the metallic vessel *A* are nickel-plated and highly polished. Such surfaces neither radiate nor absorb heat readily. Loss or gain of heat is still further prevented by the two vessels *C* and *B* of indurated fiber, as well as by the air spaces between them. A double close-fitting lid of the same material is also provided. Two liters of water for the absorption of the heat are placed in the vessel *A*, the temperature being measured by the thermometer *T*. Radiation of heat cannot be wholly prevented, however, so

that if the temperature of the water is below that of the surrounding objects, it will gain heat, while if it is above that of the surrounding objects, it will lose heat. Error from this source is compensated for by starting a determination with the water as much below atmospheric temperature as it will rise above this

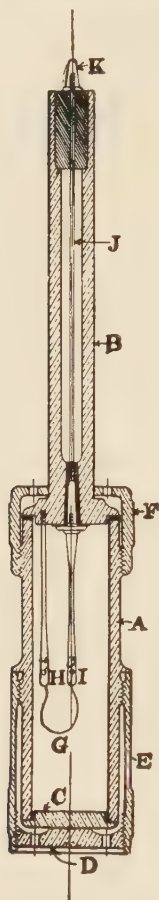


FIG. 63.

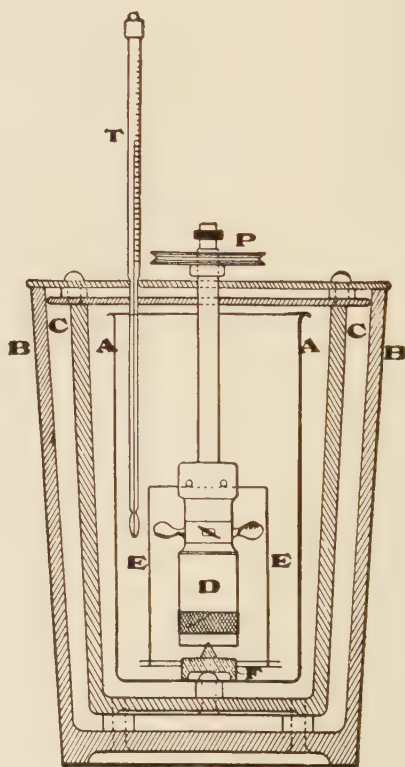


FIG. 64.

temperature after the combustion. The rate at which the water increases or decreases in temperature may also be determined, so that the amount of heat gained or lost may be calculated.

603. Water Equivalent of the Instrument.—All of the heat produced by the combustion of the fuel does not enter the water. The combustion cartridge, the containing vessel, as well as the

thermometer, absorb and retain a portion of the heat. The amount of heat lost in this manner may be easily calculated. These parts of the instrument are weighed and the water equivalent calculated by multiplying the total weight by the specific heat of the material used.* The cartridge and containing vessel in the Parr calorimeter are made of brass, specific heat 0.092. The thermometer is made of glass and mercury and only a portion is immersed in the water and is affected by the changes in temperature of the water. In order to ascertain the water equivalent of the thermometer, advantage is taken of the fact that the water equivalent of equal volumes of mercury and glass is the same. This follows from the fact that the product of the specific heat and specific gravity of those substances is the same: $2.5 \times 0.19 = 0.47$ for glass and $13.6 \times 0.034 = 0.46$ for mercury. That is, one cubic centimeter of either mercury or glass is raised one degree by .46-.47 calories of heat. The volume of that portion of the thermometer which is immersed in the water is ascertained by immersing the thermometer in a graduated cylinder partially filled with water to the same point to which it is immersed when used in the calorimeter. The volume of the portion of the thermometer which is immersed is then read directly on the cylinder.

604. Accelerators.—The use of sodium peroxide alone has not been found entirely satisfactory. The addition of small amounts of substances like potassium chlorate or a persulphate is advantageous because the oxygen in these compounds is more easily liberated, and this assists in starting the reaction which proceeds easily when the temperature is raised sufficiently to decompose the sodium peroxide. The same object is attained by the addition of substances which are more readily oxidized than the coal or other substance to be burned. Tartaric acid is such a substance. Ammonium compounds are also very easily oxidized on account of the large amount of hydrogen present. Ammonium persulphate has been found to be admirably adapted for this purpose because

* SPECIFIC HEATS.

Brass, 0.092-0.094
Glass, 0.190
Mercury, 0.034

Nickel, 0.110
Silver, 0.057
Platinum, 0.032

it contains both the ammonium radical and also the easily liberated oxygen. The term accelerator is used to designate this class of substances.

605. Correction Factors.—A correction factor must be introduced into the calculation when accelerators are used. The heat of formation of potassium chlorate is -11.9 calories for the gram molecular weight when formed from KCl and $1\frac{1}{2} \text{O}_2$, while the same constant for sodium peroxide is 119.8 when formed from Na_2O and O . When ammonium persulphate is used, heat is evolved by the combustion of the hydrogen. The correction for $\frac{1}{2}$ gram of potassium chlorate is $-.040^\circ \text{C}$., and for $\frac{1}{2}$ gram of a mixture of one part of ammonium persulphate and two parts of potassium persulphate, $-.197^\circ \text{C}$. This persulphate mixture has been found especially advantageous for use with anthracite coal.

No appreciable oxidation of nitrogen takes place in the Parr calorimeter. A correction must be introduced for sulphur and for ash. When using $\frac{1}{2}$ gram of coal, these corrections are $-.006^\circ \text{C}$. for each per cent of sulphur, and $-.001^\circ \text{C}$. for each per cent of ash. A correction of $-.008^\circ \text{C}$. must be made for each length of 10 mm . of fine iron wire.

Another correction should also be introduced when bituminous coals are burned, on account of the oxygen or hydroxyl compounds present. No such correction is necessary for anthracite coals. The corrections may be summarized as follows:

Corrections for average anthracite coals, using $\frac{1}{2}$ gram of coal, 10 grams of Na_2O_2 , and $\frac{1}{2}$ gram of persulphate mixture:

$\frac{1}{2}$ gram persulphate mixture .	0.197
1 per cent of sulphur.....	0.006
7 " " " ash	0.007
Fuse wire.....	0.008
Total.	0.218°C .,
	or 0.392°F .

Corrections for average semi-bituminous coal (not over 25 per cent volatile matter), using $\frac{1}{2}$ gram of coal, 10 grams of Na_2O_2 , and $\frac{1}{2}$ gram KClO_3 :

$\frac{1}{2}$ gram KClO_3	0.040
1 per cent sulphur	0.006
7 " " ash	0.007
4 " " combined water... ..	0.013
Fuse wire.....	0.008
Total.....	0.074° C.,
	or 0.133° F.

Corrections for average bituminous coal (over 25 per cent volatile matter):

$\frac{1}{2}$ gram KClO_3	0.040
2 per cent sulphur	0.012
10 " " ash	0.010
10 " " combined water... ..	0.033
Fuse wire.....	0.008
Total	0.103° C.,
	or 0.185° F.

EXERCISE 71.

Determination of the Calorific Value of Coal by Means of the Parr Calorimeter.

606. Electric Ignition.—Grind the coal fine enough to pass through a sieve of .25 mm. mesh or 100 to the square inch. Weigh out exactly $\frac{1}{2}$ gram and dry for 1 hour in an air-bath heated to 104°–107° C. If the coal contains less than 2 $\frac{1}{2}$ per cent of water, the drying is unnecessary. By adding cold or hot water, bring the temperature of two liters of water to about 2° F. below room temperature. Measure out exactly two liters of this water and place in the calorimeter. Transfer one full measure (10 grams) of sodium peroxide to the cartridge, which must be absolutely dry. Transfer the coal to the cartridge, brushing off the watch-crystal carefully. If the coal is anthracite, add exactly $\frac{1}{2}$ gram of the persulphate mixture. If a bituminous coal is being tested, add exactly $\frac{1}{2}$ gram of potassium chlorate. Mix the contents of the cartridge thoroughly by stirring with a rod which is afterwards well brushed off. The more recent instruments are supplied with a false cap with burnished face, which is fastened temporarily in place, and the contents of the cartridge mixed by shaking. After thorough mixing in this manner, the provisional cap is removed and the cap with stem and terminals substituted. In this way no chemical can come in contact with

the base of the terminals and produce a short circuit. The cartridge is then tapped lightly to shake all the material from the upper part of the cylinder and to settle the contents. When the electric method of ignition is used, the fine iron wire (34 American gauge) is wrapped firmly with good contact around the ends of the terminals, so as to leave a U-shaped loop extending about three-quarters of an inch below the terminals and well into the chemical mixture. If the loop is too long, it is not readily fused. The proper length of wire may be ascertained by a preliminary test without screwing the top on the cartridge. The current required is from 2 to 4 amperes and is readily obtained by placing in parallel four to eight 16-candle-power lamps in an ordinary lighting circuit of 110 volts. The current may also be obtained from 6 to 8 dry cells connected in series. The adjustment of the wire must be made before the sodium peroxide is placed in the cartridge, as it rapidly absorbs moisture. When the top has been pressed firmly in place and screwed down, the vanes are adjusted and the cartridge placed in the can of water. The cover is adjusted and the thermometer inserted so that the bulb is about half-way down in the water. The pulley on the stem is connected with the motor and the cartridge rotated to the right, or as the hands of a watch turn, so as to deflect the water downwards in the can. The thermometer is read at three-minute intervals until the readings are constant or the rise in temperature is constant. These readings must be made with the greatest care and tenths of the smallest divisions estimated as carefully as possible.

After igniting the charge by bringing the spring in contact with the revolving stem of the cartridge, the temperature rises rapidly at first, and then more slowly, until the maximum temperature is reached. The readings are made at three-minute intervals as before, until the temperature is constant or it begins to fall. The cartridge is removed and the parts unscrewed and placed in a dish of hot water to dissolve the melt. It is then rinsed thoroughly with distilled water and dried, when it is ready for another determination.

607. Ignition by Hot Wire.—If the ignition is made by means of a hot wire, the method of filling the cartridge and rotating it until the temperature is constant is the same as when the electric ignition is used. The short piece of soft iron wire is placed on a wire gauze and heated to redness in a Bunsen-burner flame and dropped quickly into the opening at the upper end of the valve. With the pincers the valve is now pressed completely down and released with a quick motion, so as to prevent the escape of heated air from the interior. During this operation the cartridge is kept revolving. The remainder of the operation is the same as when the electric method of ignition is used.

608. Calculation.—The various correction factors, as given on page 402, are subtracted from the total rise in temperature. The remainder is multiplied by 3117. This factor is obtained from the following formula:

$$\frac{\text{Total water eqv.} \times 0.73 \times \text{Corrected rise}}{\text{Weight of fuel taken}} = \text{Calorific value.}$$

Substituting the known values,

$$\frac{2135 \times 0.73 \times r}{0.5},$$

which reduces to $3117 \times r$. The product will be the calorific power of the coal in B. T. U. per pound of coal.

CHAPTER XXIX.

WATER ANALYSIS.

A CHEMICAL analysis of water is carried on by very different methods, depending on the use to which the water is to be put. These methods may conveniently be divided into two classes. In the first class are placed those methods by which the POTABILITY of a water is determined, while in the second class are included the methods by which the suitability of a water for INDUSTRIAL PURPOSES is determined. As the requirements of the various industries are somewhat diverse, the methods used in testing a water for industrial purposes cannot be so definitely stated as those employed when the water is to be used for domestic consumption.

In the latter case no poisonous substances may be present even in minute traces. The absence of lead, copper, etc., being insured, we may conveniently classify the methods commonly used into those by which the amount of ORGANIC impurities and those by which the amount of INORGANIC impurities are determined. As the commonly occurring inorganic salts, such as *sulphates*, *chlorides*, and *carbonates of lime*, *magnesia*, *the alkalies*, *iron*, etc., are not objectionable unless present in excessive amounts, only the total amount of the calcium and magnesium salts present is determined and reported as hardness of the water. If the water is classed as a MINERAL WATER, and is therefore to be used because of the inorganic salts present, a complete analysis of these must be made, as well as determinations of the organic impurities. The most important determinations for indicating the presence of organic impurities are the estimation of the amount of nitrogen in its various forms and chlorine.

SANITARY ANALYSIS.

609. Bacteriological Examination.—As has been said, the sanitary analysis consists in the determination of the organic and the inorganic impurities present. The most serious ill effect of

using impure water undoubtedly arises from taking into the system DISEASE GERMS which exist in the water. It would seem, therefore, that the examination of the water should primarily be entrusted to the *bacteriologist*. Unfortunately, it is extremely difficult, if not impossible, in the present condition of bacteriological science, to detect and identify the specific disease germs even if they undoubtedly exist in a given water. This is largely due to the fact that the great majority of the germs that exist in water are either harmless or even beneficial. The continual drinking of a water containing relatively few disease germs by a person in whose system the germ can live, ultimately results in the accumulation of the germs in sufficient quantity to produce disease.

The routine bacteriological tests generally made on water consist of a count of the total number of bacteria present and a test for the presence or absence of *B. coli*. These bacteria are almost invariably present in the intestines of human beings and other warm-blooded animals. Their presence in water is regarded as evidence of contamination with sewage, which almost always contains disease germs excreted from the body, thus rendering the water unwholesome and dangerous. The presence of an excessive number of bacteria in water also renders it deleterious to health.

610. Source of Impurities.—The chemical examination gives indirect evidence of the presence of disease germs by revealing the presence and the amount of organic matter in the water, as well as whether it is of animal or vegetable origin, and the extent to which it has undergone decomposition. As SEWAGE is undoubtedly the most common source of contamination of water with pathogenic germs, the evidence furnished by the chemist of its presence is quite sufficient to condemn a water for household use, even if the specific disease germ is not found. If the water is liable to be contaminated with sewage, it is almost certain that sooner or later it will be rendered poisonous by the presence of the germs of disease. It is evident that after organic impurities have been found in a water it is important to know their source before a decision can be reached as to the potability of a water. Whenever possible, therefore, *the chemical examination should be supplemented*

by an examination of the source of the water-supply; that is, whether it is a spring, lake, river, well, etc. If surface or underground drainage can mingle with the water, the entire region drained should be examined, if possible, for sources of contamination.

611. The Samples *must be taken with the greatest care.* As the impurities at best are present in very small amount, careless washing of the bottle, or collecting water contaminated after leaving the source of supply, may easily introduce as much impurity as was originally present. The bottles used should be thoroughly cleaned by means of strong dichromate solution and then thoroughly rinsed out with distilled water and drained. They should then be rinsed out with the water to be examined.

If water from a CITY SUPPLY is to be examined, it must be allowed to flow from the pipes a considerable time before filling the bottle, unless the water is to be examined for lead or other contamination from the pipes.

If a WELL-WATER is to be examined, the stagnant water in the pump must first be completely removed.

A sample of SPRING, RIVER, or LAKE WATER is best taken by allowing the bottle to fill after immersion some distance under the surface of the water, so as to avoid the floating surface contamination.

The TIME which may elapse between the collection of a sample and the beginning of its analysis varies with the character of the sample and other conditions. The following limits are generally safe: for fairly pure surface-water, 24 to 48 hours; and for normal ground-water, 48 to 72 hours. Polluted water requires analysis within 12 hours. A bacteriological examination should in all cases be made within 6 hours. If for any reason the examination is delayed, the sample must be preserved on ice.

PHYSICAL EXAMINATION.

The physical examination includes observations of the temperature, general appearance, color, turbidity, and the odor in hot and cold samples.

612. The Temperature should be taken at the time of collection to the nearest 0.5° Centigrade.

613. Turbidity.—The general appearance of the water should be determined by inspection in strong light after standing several

hours. Substances remaining in suspension are then classified as *turbidity on standing*, and substances settling to the bottom as *sediment*. Instead of expressing the turbidity as *none*, *slight*, *distinct*, *decided*, etc., it is advisable to use the NUMERICAL STANDARDS recently introduced by which the turbidity is expressed in parts of silica per one million. The stock suspension of silica is prepared as follows: Diatomaceous earth, as free from amorphous silica and sponge spicules as may be obtained, is washed with water to free it from any soluble salts, and ignited to remove any organic matter. It is then treated with warm dilute hydrochloric acid, and washed with successive portions of distilled water until free from acid. The material, now composed of practically pure diatomaceous frustules, is ground to an impalpable powder in an agate mortar, sifted through a sieve that has 200 meshes to the inch, and dried in a desiccator. One gram of this prepared diatomaceous earth in 1 liter of distilled water gives the stock suspension which has a turbidity of 1000, i.e., contains 1000 parts of silica per million.

STANDARDS for comparison should be prepared from this stock suspension by dilution with distilled water. For turbidity readings below 20, standards of 0, 5, 10, 15, and 20 are kept in gallon bottles made of clear white glass; for readings above 20, standards of 20, 30, 40, 50, 60, 70, 80, 90, and 100 are kept in 100-c.c. Nessler jars, approximately 20 mm. in diameter.

COMPARISON OF THE WATER under examination with the standards is made by viewing them sidewise towards the light, looking at some object and noting the distinctness with which the margins of the object can be seen. The standards are kept stoppered, and both sample and standards are thoroughly shaken before making the comparison. In order to prevent any bacterial or algæ growths from appearing in the standards, a small amount of bichloride of mercury may be added to them.

614. The Color of the water is measured by comparison with the color of a solution of platinum and cobalt and is expressed in parts of platinum per million. A standard solution which has a color of 500 is made by dissolving 1.246 grams potassium platinic chloride ($\text{PtCl}_4 \cdot 2\text{KCl}$), containing 0.5 gram platinum, and 1 gram of crystallized cobaltous chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), containing 0.25 gram of cobalt in water, with 100 c.c. concentrated hydrochloric

acid, and making up to 1 liter with distilled water. By diluting this solution standards are prepared having colors of 0, 5, 10, 15, 20, 25, 30, 35, 40, 50, 60, and 70 parts per million. These are kept in 100-c.c. Nessler jars of such diameter that the liquid has a depth between 20 and 25 cm. and is protected from dust.

The color of a sample is observed by filling a similar tube with the water and comparing it with the standards. The observation is made by looking vertically downwards through the tubes upon a white surface placed at such an angle that light is reflected upwards through the column of liquid. The reading is recorded to the nearest unit. Waters that have a color darker than 70 are diluted before making the comparison, in order that no difficulties may be encountered in matching the hues. Water containing matter in suspension is filtered until no visible turbidity remains.

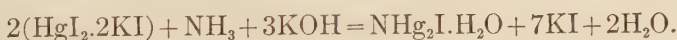
615. The Odor of the water both hot and cold is observed. To obtain the odor of the cold water the sample in the large collecting-bottle, which should be about one-half or two-thirds full, is shaken vigorously, the stopper removed, and the nose immediately placed to the mouth of the bottle. To obtain the odor of the hot water it is poured into a moderately large beaker until it is about one-third full. The beaker is covered with a watch-crystal and the water is rapidly brought to a boil. It is immediately removed from the source of heat and allowed to cool for about five minutes. The beaker is then shaken with a rotary motion, the watch-crystal slipped to one side, and the odor observed. The odor is expressed by such terms as the following: *vegetable, aromatic, grassy, fishy, earthy, mouldy, musty, disagreeable, peaty, and sweetish*. The *intensity* of the odor is usually indicated by the numbers 1, 2, 3, 4, and 5, 1 indicating very faint; 2, faint; 3, distinct; 4, decided; and 5, strong.

CHEMICAL EXAMINATION.

The first determination carried out should be that of the amount of nitrogenous organic matter present, as this material is continually undergoing changes, and the condition in which the nitrogen exists is taken as an index of the source of the contamination, and the time which has elapsed since it has been introduced.

616. The Nitrogen may exist as so-called ALBUMINOID NITROGEN, AMMONIA, NITRITES, or NITRATES. The albuminoid nitrogen is undoubtedly present as part of a class of complex organic compounds, called proteins, which may have been derived from plant, but more likely animal, tissues which are present in the water. These tissues undergo a more or less rapid decomposition or putrefaction by which the nitrogen assumes for the most part the condition of FREE AMMONIA, which may then be oxidized to nitrites or nitrates. The presence of the unstable nitrites generally indicates the presence of sewage or other organic matter in a state of decomposition. While nitrates may be produced by the oxidation of organic nitrogen, this is by no means the only source, since the atmosphere and the soil contain considerable amounts of nitric acid or nitrates, which are dissolved by the rain. The amount of nitrates in a surface-water increases with the density of population in the region drained.

617. Determination of Free and Albuminoid Ammonia.—Ammonia is determined by means of the so-called NESSLER SOLUTION, to which a brown color is given by very small amounts of ammonia or ammonium salts. The reagent consists of a strongly alkaline solution of the double iodide of potassium and mercury, $\text{HgI}_2 \cdot 2\text{KI}$. Ammonia produces in this solution a dark-brown coloration or precipitate of dimercuric ammonium iodide, $\text{NHg}_2\text{I} \cdot \text{H}_2\text{O}$, according to the following equation:



The depth of the color produced is proportional to the amount of ammonia present, so that by comparison with solutions containing known amounts of ammonia, the amount of ammonia present in a given solution may be determined, the solution containing the known amount of ammonia being so adjusted that its color exactly matches the solution containing the unknown amount.

618. Preparation of Nessler Solution.*—Dissolve 61.75 grams of potassium iodide in 250 c.c. of ammonia-free water and add a cold solution of mercuric chloride which has been saturated by

* D. D. Jackson, Tech. Quar., XIII, No. 4, Dec. 1900, p. 320.

boiling with excess of the salt. Pour in the mercury solution cautiously and add an amount just sufficient to make the color a permanent bright red, which will require about 400 c.c. Dissolve the red precipitate by adding exactly .75 gram potassium iodide. Then add 150 grams of potassium hydrate dissolved in 250 c.c. of water and dilute the solution to 1 liter. Mix thoroughly and allow the solution to stand until any precipitate formed has settled, leaving a pale straw-colored solution which is siphoned or decanted off into another bottle for use. The solution improves with age. Its sensitiveness is increased by adding mercuric chloride and decreased by adding potassium iodide. The 2-c.c. portions used for each test must be measured quite carefully as the depth of color produced with a given amount of ammonia depends to a certain extent upon the amount of Nessler solution used.

The following solutions will also be required:

619. Alkaline Potassium Permanganate Solution.—Dissolve 200 grams of solid caustic potash* and 8 grams of potassium permanganate in 1250 c.c. of distilled water. Boil the solution down to 1 liter and preserve for use.

620. Sodium Carbonate Solution.—Dissolve 50 grams of the pure salt in 300 c.c. of ammonia-free water.

621. Standard Ammonia Solution.—Dissolve 1.5701 grams of pure dry ammonium chloride in ammonia-free water and dilute to 500 c.c. 1 c.c. of this solution will contain 1 mg. of ammonia. 10 c.c. should be diluted to 1 liter with ammonia-free water. 1 c.c. of this solution will contain .01 mg. of ammonia and is the standard solution used.

622. Ammonia-free Water.—Ordinary distilled water generally contains considerable amounts of ammonia. It may be tested by adding 2 c.c. of Nessler solution to 50 c.c. of the water placed in a NESSLER TUBE. These tubes are made of colorless glass and contain 50-c.c. when filled to a mark near the top. A tube of suitable proportions has a diameter of 1.7 cm. and a height of 21 cm. to the 50-c.c. mark. If after standing five minutes no trace of a yellow tint is developed in the water it may be used without purification. Generally, however, it must be freed from ammonia.

* If caustic potash free from carbonates is used, the bumping so apt to occur while boiling an alkaline solution will be very much reduced.

This may be done by nearly filling a large glass retort or a suitable copper or tin vessel with distilled water to which some of the alkaline potassium permanganate solution has been added. A glass or block-tin condenser is attached and the water is distilled until 50-c.c. portions tested with the Nessler solution are found free from ammonia. The distillate is then collected in a clean bottle for use.

The distilled water may also be freed from ammonia by adding enough bromine water to color it distinctly and then boiling until the excess of bromine is expelled. The boiling may be omitted if a drop of caustic soda is added to the water tinted with bromine, and after standing ten minutes the undecomposed hypobromite removed by adding a little potassium iodide.

The preparation of the ammonia-free water and all ammonia determinations must be carried out in a room whose atmosphere is free from ammonia and ammonium salts. The ordinary laboratory is, therefore, not suited to the purpose.

DETERMINATION OF FREE AMMONIA.

623. Distillation.—A liter flask is connected by means of a short piece of rubber tubing or a rubber stopper with a Liebig condenser. A tubulated glass retort capable of holding a liter of solution is also very convenient for this purpose, as the reagent can be introduced through the tubulure. The stem of the retort may be introduced into the end of the condenser-tube and a tight joint made by means of a short piece of rubber tubing. The distillate is led into the Nessler tubes by means of an adapter.

Although the apparatus is thoroughly cleaned before being set up, to completely remove ammonia about 200 c.c. of ammonia-free water is introduced into the retort and 10 c.c. of the sodium carbonate solution added. The solution is boiled and the first 50 c.c. of the distillate discarded while the second 50-c.c. portion is tested for ammonia by adding 2 c.c. of the Nessler solution. If no color develops after standing five minutes the apparatus may be considered free from ammonia and the water to be analyzed may be introduced into the retort. Unless the water contains an unusual amount of ammonia 500 c.c. will be found to be a

convenient amount. A preliminary test may be made by adding 2 c.c. of Nessler solution to 50 c.c. of the water to be tested. The color developed is compared with the color produced by adding 0.5 c.c. of the standard ammonia solution to 50 c.c. of ammonia-free water. If the color produced in the tube containing the water to be analyzed is the darker, less than 500 c.c. of the water should be placed in the retort and the difference made up by ammonia-free water.

624. Nesslerizing.—The distillate is collected in the Nesslerizing tubes, which are placed in a rack in order after being filled to the 50-c.c. mark. The flame of the Bunsen burner should be so adjusted that 50 c.c. are distilled in about eight minutes. As soon

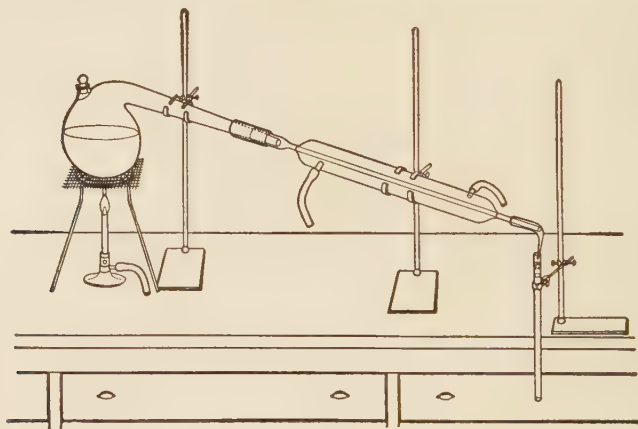


FIG. 65.

as the second tube is filled and has come to room temperature it is Nesslerized. 2 c.c. of the Nessler solution is added. Several clean Nessler tubes are taken and carefully measured amounts of the standard ammonia solution added from a burette, such as 1 c.c., 2 c.c., 3 c.c., etc. The tubes are then filled with ammonia-free water to the 50-c.c. mark, and 2 c.c. of the Nessler solution added to each tube. After a little practice the solutions may readily be mixed by shaking with the hand. Long clean glass rods may also be used for stirring the contents of the tubes.

The colors are compared by holding two tubes in the hand and looking through the length of the tubes, which are held over a white paper or piece of porcelain in a good light. If the color of a

tube does not match that of any of the standards made, others must be made with the amount of standard ammonia solution judged necessary until the color of the unknown ammonia-tubes have been matched. After adding the Nessler solution, five minutes must elapse before comparing the color, as it does not develop instantly. After being fully formed the color is quite permanent, so that a set of standard tubes may be used during a day's work without error. A permanent set of standard tubes has been devised by D. D. Jackson.* The temperature of the water may vary between 18° and 25° without material change in depth of color.

If the ammonia in the second tube corresponds to 1 c.c. or less of the standard solution, further distillation may be dispensed with. Otherwise 50-c.c. portions must be collected until this limit is reached. Usually three 50-c.c. portions are collected. If the ammonia in the second tube corresponds to 2 c.c. or less of the standard solution, the first tube may be Nesslerized in the same manner as the second. If the second tube contains a greater amount of ammonia, a measured portion of the first tube must be taken and diluted with ammonia-free water and Nesslerized. Or the contents of the first and third tubes may be mixed and 50 c.c. of the mixture Nesslerized. In no case should the color of a tube be read which responds to more than 10 c.c. of the standard ammonia solution.

625. Calculation.—The various amounts of ammonia found in the different tubes are added and the result stated in parts per million. If, for instance, the first tube was found to match a tube containing 9 c.c. of standard ammonia solution, the second 3 c.c., the third 1 c.c., and the fourth free from ammonia, then, as 1 c.c. is equal to .01 mg. of ammonia, the total amount of ammonia would be $.09 + .03 + .01 = .13$ mg. As 500 c.c. of the water was taken and as 1 mg. is the millionth part by weight of a liter of water, the amount of *free ammonia* present in the water would be .26 parts per million.

* Tech. Quar., Vol. XIII, No. 4, Dec. 1900, p. 320.

DETERMINATION OF ALBUMINOID AMMONIA.

626. Distillation.—When all the free ammonia has been distilled off, which is usually the case when 150 c.c. of distillate has been collected, 50 c.c. of the alkaline permanganate solution is added and the distillation continued, 50-c.c. portions being collected in the Nessler tubes and the ammonia determined and calculated exactly as given for free ammonia.

The albuminoid ammonia does not always come off as readily as the free ammonia. This is undoubtedly due to the greater or less difficulty of decomposing organic matter from different sources. Organic matter derived from vegetables is generally decomposed with more difficulty than the contamination derived from partially decomposed animal refuse as found in sewage. Each 50-c.c. portion of the distillate for albuminoid ammonia must therefore be tested to be sure that all of the ammonia has been obtained, the solution in the retort being boiled nearly dry. As it is almost impossible to obtain all of the albuminoid ammonia from many waters, especially highly colored surface-waters, the practice is growing of collecting five 50-c.c. portions of the distillate for the albuminoid ammonia. In this way comparative results are obtained which are of almost as great value as if the total amount of albuminoid ammonia were obtained in each case. Much time and labor are also saved. About one-half of the total organic nitrogen will generally be obtained in the 250 c.c. of distillate.

DETERMINATION OF NITRITES.

A colorimetric process similar to that used to determine ammonia is in use for the estimation of the amount of nitrites present. Of the several methods which have been suggested, that of GRIESS will be given. It depends on the fact that a red coloration is produced when a solution of SULPHANILIC ACID and NAPHTHYLAMINE HYDROCHLORIDE are added to an acidified solution of a nitrite. This test is said to be capable of showing one part of nitrogen as nitrite in one thousand million parts of water.

The following reagents must be prepared:

627. Sulphanilic Acid.—Dissolve 0.8 gram of the acid in 100 c.c. of hot water.

628. Naphthylamine Hydrochloride.—Dissolve 0.8 gram of the salt in 100 c.c. of water and 1 c.c. of strong hydrochloric acid. Decolorize the solution by adding a little powdered charcoal. Place the solution in a glass-stoppered bottle with the charcoal and filter as required for use.

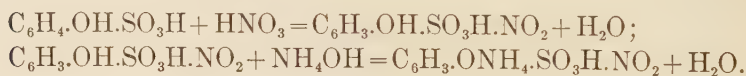
629. Standard Solution of Sodium Nitrite.—Pure silver nitrite is prepared by mixing a warm concentrated solution of 8 parts of sodium nitrite with a warm concentrated solution of 16 parts of silver nitrate. The precipitate, when cold, is washed with cold water and quickly dried over a water-bath with as little exposure to the light as possible. Weigh .1091 gram of the dry nitrite and dissolve in warm water. Add a slight excess of pure sodium chloride and dilute to 1 liter. After allowing the silver chloride to settle, draw out 10 c.c. and dilute to 1 liter. This will give a standard solution, 1 c.c. of which will be equal to .001 mg. of nitrogen as nitrite

630. The Determination is carried out as follows: 100 c.c. of the water to be examined are placed in a cylinder capable of holding 100 c.c., which is made of the same kind of colorless glass as the Nessler tube, although a shorter and wider tube is found convenient, a suitable size being 3 cm. in diameter and 13.2 cm. from the bottom to the 100-c.c. mark. One drop of concentrated hydrochloric acid is added and then 2 c.c. of the sulphanilic acid solution and 2 c.c. of the solution of hydrochloride of naphthylamine. After mixing well, the tube is tightly stoppered and allowed to stand for ten minutes until the color is fully developed. In the meantime tubes are prepared containing known amounts of nitrite, 1 c.c., 2 c.c., 3 c.c., etc., of the standard nitrite solution being added to tubes containing 100 c.c. of ordinary distilled water, or, still better, water redistilled as directed for ammonia-free water. After the addition of 2 c.c. of each reagent to each of the color solutions and a drop of hydrochloric acid, and allowing the tubes to stand for twenty minutes, the colors of the known and the unknown solutions are compared and the amount of nitrogen present per million parts is computed. If 100 c.c. of the water

is taken and the color is matched by the tube containing 3 c.c. of the standard nitrite solution, the water contains .03 part per million of nitrogen as nitrite. As this test is extremely delicate, it is advisable to make a blank determination to detect accidental contamination which at times arises from nitrous fumes in the air.

DETERMINATION OF NITRATES.

This determination also is carried out by a colorimetric process, the yellow AMMONIUM SALT OF NITROPHENOL-SULPHONIC ACID* being produced when the water to be examined is evaporated to dryness and treated with PHENOL-SULPHONIC ACID and ammonia. The following reactions take place:



The intensity of the color developed is compared with the color produced by the same process in water containing a known amount of nitrate.

The following solutions are required:

631. Phenol-sulphonic Acid.—In 148 c.c. of pure concentrated sulphuric acid 24 grams of pure phenol are dissolved by heating on the water-bath and 12 c.c. of distilled water added.

632. Standard Potassium Nitrate Solution.—0.722 gram of pure dry potassium nitrate is weighed out and dissolved in 1 liter of distilled water. 10 c.c. of this solution are evaporated to dryness, 2 c.c. of the phenol-sulphonic acid added, and quickly and thoroughly mixed with the residue by means of a glass rod. The mixture is dissolved in distilled water and the solution diluted to 1 liter.

The color-tubes for comparison are prepared by measuring out portions of this solution into 100-c.c. tubes of the size used for the nitrite determination, adding 5 c.c. of strong ammonia and diluting to 100 c.c. These standards are permanent for several months if the tubes are well corked with stoppers from which the coloring matter has been extracted by boiling water. 1 c.c. of the dilute nitrate solution is equal to .001 mg. of nitrogen as nitrate.

* Jour. Am. Chem. Soc., XXVI, 388.

633. The Determination is carried out as follows: 25 c.c. of the water to be analyzed are taken, or, if the amount of nitrate present is small, 50 or even 100 c.c. are taken and evaporated to dryness. The residue is treated with 1 c.c. of the phenol-sulphonic acid and well mixed by stirring with a glass rod. 10 c.c. of distilled water are added and then 5 c.c. of strong ammonia. The solution is washed into a 100-c.c. tube and diluted to the mark with distilled water. The depth of color is now compared with that of the standard color-tubes containing various amounts of the standard nitrate solution.

When the color has been exactly matched, the parts per million of nitrogen as nitrate are calculated. If, for instance, 50 c.c. of the water were taken and the color was matched by the standard color-tube containing 3 c.c. of the dilute nitrate solution, then 50 c.c. of the water would contain .003 mg. of nitrogen as nitrate, which would be .06 part per million. If 25 c.c. of a water had been taken, the result would be .12 part per million if the color produced were matched by a color-tube containing 3 c.c. of the standard nitrate solution.

DETERMINATION OF THE OXYGEN REQUIRED TO OXIDIZE ORGANIC MATTER.

The methods already given have shown the amount of nitrogen present in a given water in the four forms: ammonia, nitrous and nitric acid, and albuminoid substances. A very simple method is in use for the determination of the amount of carbon present. It consists in ascertaining the amount of permanganate required to oxidize the organic matter present. The water is boiled for ten minutes with sulphuric acid and an excess of standard potassium permanganate solution. The excess of the permanganate is then titrated back with standard oxalic acid.

634. Errors.—It is evident that by this process any substance other than carbonaceous material capable of being oxidized under the conditions will also reduce the permanganate. On the other hand, the oxidation of the organic matter present may not be complete. It has indeed been shown that the extent to which different kinds of organic matter are oxidized varies greatly. As the method, therefore, is an empirical one, the conditions of the oxidation must be rigidly adhered to. If this is done, very con-

stant results are obtained and the method has shown itself of value in forming a judgment of the amount of organic matter in the water, as other oxidizable substances are rarely present. Ferrous iron and sodium chloride are the only common exceptions. The iron is quickly precipitated as ferric oxide after a few hours' exposure of the water to the air.

If a considerable amount of SODIUM CHLORIDE is present, a correction must be applied as found by a blank test. Sodium chloride is added to distilled water until there is present the amount of chloride which has been found in the water being examined. The oxidation with the permanganate is then carried out in the same manner as when the water was tested. The amount of permanganate required is subtracted from that used in testing the water.

635. The Following Solutions are required and are made with water free from organic matter. This is prepared by adding a little potassium permanganate and caustic alkali to distilled water and redistilling it. The first portions of the distillate are discarded. The steam or distilled water should not come in contact with rubber or other organic matter. A suitable distilling apparatus may be made by connecting a retort with a Liebig condenser by inserting the tube of the retort into the inner tube of the condenser as shown in Fig. 65, page 414, and packing the joint with ignited asbestos instead of the rubber connection.

636. Potassium Permanganate Solution is made by dissolving .3953 gram of the pure salt in 1 liter of the redistilled water. 1 c.c. of this solution will contain 0.1 mg. of available oxygen.

637. Oxalic Acid Solution is made by dissolving .7875 gram of the pure recrystallized and carefully dried salt in 1 liter of water. If this salt as well as the permanganate are pure, these solutions will be exactly equal. They should be titrated against each other by measuring out 10 c.c. of the oxalic acid, adding 10 c.c. of dilute sulphuric acid and 200 c.c. of the redistilled water. The whole is heated to boiling and the potassium permanganate solution introduced until a faint, permanent pink coloration is produced. Neither the oxalic acid nor the permanganate solutions are permanent and must be made up fresh or standardized from time to time.

Dilute sulphuric acid is made by diluting 1 part of concentrated acid with 3 parts of the redistilled water.

638. The Determination is carried out by placing 100 c.c. of the water to be tested in a flask and adding 10 c.c. of the dilute sulphuric acid. The standard potassium permanganate solution is introduced from a burette until the water is colored. It is heated to boiling and more permanganate is introduced if the color fades. If brown flakes of manganese dioxide are formed, more dilute sulphuric acid must be added. The boiling is continued for five minutes. An excess of oxalic acid is then introduced and titrated back with the permanganate solution. The volume of oxalic acid introduced is subtracted from the total amount of the permanganate solution used, and the number of milligrams of oxygen consumed is calculated.

The result is stated in parts of oxygen required per million parts of water.

If the amount of organic matter in the water is considerable, less than 100 c.c. must be taken for this determination. The volume should in each case be made up to 100 c.c. with the redistilled water. As the success of this determination is assured only by working under absolutely fixed conditions, the determination should be repeated several times until constant results are obtained.

DETERMINATION OF CHLORIDES.

The chlorine in natural waters exists for the most part in the form of sodium chloride, and as such is harmless unless present in very large amounts. As considerable amounts of salt are used very generally in articles of food, it is present in large amounts in urine, and therefore in sewage. For this reason the amount of chlorides present is used as an index of the amount of contamination of the water. As almost all natural waters, including rain-water, contain chlorides in greater or less amount, only that amount of chlorides which is above the average of similar but pure waters can be used as an argument for condemning a water as contaminated.

639. Silver Nitrate Solution.—The chlorine is determined volumetrically, using a standard silver nitrate solution with potassium chromate as indicator, as described in Chapter XXVI. The silver

nitrate solution is made of such a strength that 1 c.c. is equal to 1 mg. of chlorine. For this purpose 4.7938 grams of pure silver nitrate are weighed out and dissolved in a liter of water. The potassium chromate indicator is made by dissolving 5 grams of the pure salt in 100 c.c. of distilled water.

640. The Determination is carried out by placing 100 c.c. of the water to be examined in a porcelain dish and adding 1 c.c. of the indicator. The silver nitrate solution is added until a faint permanent red color is produced. This red color should be removed by adding a pinch of sodium chloride or a drop or two of a chloride solution and the titration repeated, using the first solution for comparison. This solution will have a pure-yellow color with a white silver chloride precipitate equal to that obtained in the second titration. The end-point may be made still sharper by preparing a solution of distilled water containing 1 c.c. of the indicator, through which the solution being titrated may be observed.

As an appreciable amount of the silver nitrate solution may be required to produce the color indicating the end-point, a blank determination should be made by adding 1 c.c. of the indicator to 100 c.c. of distilled water and then adding silver nitrate solution until the red color is observed. The volume of silver nitrate added should be subtracted from the amount added to the water being tested.

When the amount of chlorides present is very small, or great accuracy is required, an amount of water greater than 100 c.c. should be taken and evaporated down to a bulk of about 100 c.c. after the addition of 0.1 c.c. of a saturated solution of sodium carbonate. This solution is then titrated as already given. If the water contains considerable coloring-matter, so that after concentration the color of the indicator cannot be observed, the coloring-matter may be removed before concentration by shaking the water with some freshly precipitated aluminum hydrate and filtering before measuring out the portion for evaporation. If the water is acid, it must be neutralized with sodium carbonate.

641. The Determination of Hardness in water, both temporary and permanent, has already been given in Chapter XXI, page 269.

642. Determination of Total Solids.—This determination is conducted by evaporating a measured volume of the water, 100

to 500 c.c. being usually taken, to dryness in a weighed platinum dish. Various temperatures from 105° to 180° have been used for drying the residue before weighing, 103° having now been fixed as the standard temperature. After weighing, the organic matter is volatilized by gently igniting the residue. When the carbon has been burned off, the alkaline-earth metals are reconverted to carbonates by treatment with carbonic-acid water, and after evaporating and gently igniting, the residue is again weighed. The loss in weight was formerly reported as ORGANIC MATTER.

It is generally recognized that the results of this determination are at best but roughly approximate. During the evaporation considerable organic matter may be lost, still more being volatilized if the residue is dried at 180°; while if the residue is dried at 105°, much water will be retained if hygroscopic salts, such as calcium chloride, are present. During the ignition this water will be expelled together with considerable amounts of sodium chloride, if this commonly occurring salt is present. The LOSS ON IGNITION is therefore considered of very little value, the chief reason for igniting the residue being to observe the amount of carbonization which takes place. The blackening of the residue by the formation of carbon, which subsequently burns off, is taken as an indication of the presence of organic matter, even if the loss in weight is inconsiderable; while the absence of a charred residue indicates the absence of organic matter, even if considerable loss in weight occurs. The presence of nitrates is indicated by sparking of the carbon on ignition. On account of the difference in practice, the *temperature at which the total solids were dried should be stated in reporting the analysis.*

BACTERIOLOGICAL EXAMINATION OF WATER.

643. Bacteria Present in Water.—All natural waters contain varying numbers of bacteria which are microscopic single-celled organisms generally living on organic matter. The bacteria which feed on living organic matter, and are therefore parasitic, constitute the class of disease germs. This class is far less numerous than the bacteria which live on dead matter and frequently cannot exist for any length of time out of their living host. Only a few of this class can multiply or even live in water, the most

common being *B. typhi*, which produces typhoid fever when it secures a foothold in the human system. Dysentery and similar intestinal diseases are produced by bacteria which are carried by water, but which have not been identified and studied. Another bacterium, *B. coli*, which is almost always present in the intestines of healthy human beings and other warm-blooded animals, can also live in water. The presence of this bacterium in water is therefore taken as evidence of sewage contamination.

Such water is always regarded as unwholesome, since disease germs from the human system may at any time be present in the water. *B. typhi* will almost certainly be present at times in such water if sewage is the source of contamination, because cases of typhoid fever may always be found in any large community.

644. Test for *B. Coli*.—Fortunately a very simple method of testing for *B. coli* has been devised. During its life activity, this bacterium decomposes carbohydrates with the production of a gas which is mainly hydrogen, with 25 to 40 per cent of carbon dioxide. Bile has the property of inhibiting the growth of other gas-forming bacteria. The sample of water is therefore mixed with bile and lactose and kept at a temperature of $37\frac{1}{2}^{\circ}$ C. for 48 hours. If gas is evolved during this incubation period, the water almost certainly contains *B. coli*. An idea of the number of these organisms present can be obtained by making three tests, using respectively .1 c.c., 1 c.c., and 10 c.c. of the water. The test is made in two test-tubes of such a size that the smaller one can be inverted within the larger one.

645. Bacterial Count.—In addition to the test for *B. coli*, the total number of bacteria in a water is determined. An excessive number of bacteria in a water indicates contamination with sewage or other decomposing animal or plant tissue, and renders the water unfit for consumption. This test is made by adding a measured amount of the water to a plate containing a sterile nutrient medium which is composed of meat extract and peptone to nourish the growing bacteria, and gelatin or agar-agar to make a semi-solid media in which the bacteria will remain fixed. Each bacterium develops a colony around it, which ultimately becomes visible to the eye under only very slight magnification. By counting these spots or colonies, the number of

bacteria originally present in the water can be ascertained. This determination is only approximate, as all of the bacteria do not grow under the conditions of incubation sufficiently to be counted. All material used must be thoroughly cleaned and sterilized by heat, so as to kill all organisms present before the water to be tested is added.

EXERCISE 72.

Bacterial Count.

646. Sterilization of Apparatus.—Clean thoroughly 12 test-tubes and insert firmly a plug of cotton. Clean 6 Petri dishes and 6 one-c.c. pipettes, also 2 small glass-stoppered bottles. Place the pipettes in a copper tube having a close-fitting cap, or in a large test-tube closed with a plug of cotton. Sterilize this apparatus by placing it in an air-oven heated to 150° for 1 hour. Prepare sterile water by nearly filling a 250-c.c. flask with distilled water and boiling vigorously for 15 to 20 minutes. Insert a plug of cotton and allow to cool.

647. Preparation of Nutrient Gelatin.—Place 500 grams of lean beef in a large beaker or flask, and add 1000 c.c. of distilled water. The meat must be as free as possible from fat and chopped fine or run through a sausage grinder. The beaker or flask is weighed and distilled water added to make up the loss by evaporation after standing 24 hours. Place a piece of new cotton flannel, with the wool side up, in a large funnel and cover with a layer of clean cotton wadding. Filter the meat infusion through the flannel, squeezing out the last portions. It is advisable to place a second smaller funnel containing the same filtering medium below the first funnel, so that the filtered solution from the first funnel passes through the second, thus giving a very clear solution. Allow the solution to flow into the inner vessel of an agate-ware double boiler of at least two quarts capacity. This vessel should be weighed empty as well as after receiving the meat infusion. Add an amount of Witte's peptone equal to 1 per cent of the weight of the infusion, and 10 per cent of the best quality of sheet gelatin (gold label). Dissolve the peptone and gelatin by stirring with a thermometer and heating the solution, not allowing the temperature to rise above 60° C. For this purpose the outer vessel only of the double boiler is heated with the Bunsen burner, the inner vessel being surrounded by the hot water. After the gelatin is dissolved, the water in the outer vessel is brought to a boil and kept boiling for 30 minutes, the inner vessel being covered.

648. Adjusting the Acidity.—After the boiling has continued for 20 minutes, withdraw 5 c.c. of the solution with a pipette and place in a porcelain dish or casserole. Add 45 c.c. of distilled water and boil for 1 minute over the Bunsen-burner flame. Add 1 c.c. of phenolphthalein solution

and titrate while hot (preferably while boiling) with N/20 caustic soda. Add the soda solution until within a drop or two of the end-point. Cool by standing the dish in cold water, and if a distinct pink color does not develop, add the soda solution drop by drop until the end-point is reached.

So much of the acid in the solution must be now neutralized that the amount of acid remaining in 1000 grams will neutralize 10 c.c. of normal caustic-soda solution. The calculation of the amount of soda to be added is made as follows: If the 5-c.c. portion titrated required $4\frac{1}{2}$ c.c. of the N/20 soda solution, and the weight of the solution is 950 grams, the entire solution will require 855 c.c. of the N/20 soda, or 42.7 c.c. of normal soda. As the acid equivalent to 10 c.c. of normal soda solution must be left free, 32.7 c.c. of normal soda solution is added.

To coagulate finely suspended matter so that the solution may be filtered clear, the white of an egg is added at this point. The solution is cooled to 60°–70° by immersing the containing vessel in cold water, and the white of an egg added with stirring; it is then heated in the double boiler and finally boiled for 2 minutes over the free flame, with constant stirring. Weigh and add distilled water to make up for loss by evaporation. Take out 5 c.c. and titrate with N/20 sodium hydroxide and calculate the acidity as before. If the acidity per 1000 grams is less than 8 c.c. or more than 12 c.c. of normal acid, acid or alkali should be added to bring the acidity to the standard 1 per cent. Take out another 5-c.c. portion and titrate a third time to ascertain if the adjustment of the acidity has been correctly carried out.

649. Sterilization of the Culture Medium.—Filter the solution again through absorbent cotton and cotton flannel, passing the filtrate through the filter until clear. The nutrient gelatin must now be measured off in 10-c.c. portions into the sterilized test-tubes closed with cotton plugs. For this purpose a glass tube graduated every 10 c.c. is convenient. The cotton plug is removed from a sterilized test-tube and held between the first and second finger and again inserted into the test-tubes as soon as the 10-c.c. portion of gelatin has been added. The gelatin should not be allowed to touch the upper portion of the test-tube, which is set aside in an upright position to cool. When all of the gelatin has been measured out into test-tubes, it is sterilized by heating for 5 minutes in an autoclave at 120°, which is the temperature of steam at 15 pounds pressure. The tubes of gelatin must be kept in an ice-chest. If the gelatin has not been completely sterilized, colonies will make their appearance in a few days.

650. Count of Bacteria.—To make the count of bacteria in water, the sample must be taken in a sterilized glass-stoppered bottle. It is advisable before sterilization to cover the stopper with tin-foil to prevent entrance of bacteria with the dust from the air; 1 c.c. is withdrawn with a sterilized pipette and transferred to a sterilized test-tube, and 9 c.c. of sterilized water added. This gives a dilution of 1 to 10. By diluting this solution

in the same manner, a dilution of 1-100 is obtained. A clean pipette must be used for each dilution. To one of these dishes 1 c.c. of the sample of water is transferred; to the second dish 1 c.c. of the 1-10 dilution, and to the third dish 1 c.c. of the 1-100 dilution. Tubes of the nutrient gelatin are melted by placing in warm water, the plug of cotton removed, the open end of the test-tube sterilized by passing it through the flame of a Bunsen burner, and the gelatin poured into three sterilized Petri dishes. The covers are raised only when pouring in water or gelatin, so as to prevent entrance of bacteria from atmospheric dust. The water and nutrient gelatin are mixed by slightly tilting the dish, so that the contents flow from one side to the other. The dish is then placed in a horizontal position in a thermostat or refrigerator kept at about 20° C. After 48 hours the number of colonies on the plate are counted. If the number is not over 200, the total number may be counted. If the number is large, some counting device must be employed. This generally consists of a plate marked off in sections or other divisions, so that the total number of divisions covered by the plate may be counted, and the average number of colonies per division is obtained by counting the number of colonies in several divisions, so as to obtain a fair average of the number per division. Small specks of dust must not be mistaken for colonies which are circular in shape. The count must generally be made with a small magnifying lens. When the colonies are small it is sometimes advisable to allow the sample to incubate for 72 hours. This fact should be stated, however, in reporting the analysis. The best results are generally obtained by counting the colonies on plates containing about 200.

651. Preparation of Nutrient Agar-agar.—When this medium is prepared the meat is soaked in one-half the quantity of water, that is, 500 c.c. Fifteen grams of thread agar are dissolved in 500 c.c. of water by boiling for one-half hour. The loss of water is then restored and the infusion allowed to cool to about 60° C. The remaining operations are identical with those used in preparing gelatin, except that 2 per cent of Witte's peptone is dissolved in the filtered meat infusion, after which the agar is added to the meat infusion, care being taken to keep the temperature below 60° C.

The samples of water are plated as described for gelatin. It is necessary, however, to heat the agar to a higher temperature in order to melt it. It should be cooled to about 40° before pouring on the plate. The plates are incubated at body temperature (37½°-40° C.) for 48 hours. The number of colonies obtained is usually higher than with gelatin. It is advisable to use porous earthenware covers with agar to prevent the spreading of colonies by the condensation of water.

EXERCISE 73.

Test for B. Coli.

Obtain a quantity of fresh ox-bile. Place in a flask and sterilize by heating in an autoclave at 15 pounds pressure for 20 minutes, or heat in steam for one-half to three-quarters of an hour. Filter through cotton and add 1 per cent of lactose. Add a sufficient amount of the bile to a large test-tube containing an inverted smaller test-tube, so that the bile will fill the small tube and act as a seal at the bottom. Fill other test-tubes in the same manner until all the bile has been utilized, and plug with cotton. Sterilize in an autoclave at 15 pounds pressure for 5 minutes. The air in the smaller tube will be expelled by the high temperature, and the steam produced, so that on cooling, the bile will entirely fill the smaller tube. Cool and store in a cool place.

Take three of these tubes and add, with sterilized pipettes, 0.1 c.c., 1 c.c., and 10 c.c. of the water to be tested. Incubate at $37\frac{1}{2}^{\circ}$ C. for 48 hours. The presence of gas in the small tube is evidence of the presence of B. coli in the water.

INTERPRETATION OF THE RESULTS OF A SANITARY WATER ANALYSIS.

No definite limits can be set for the amount of chlorides, nitrogen, or other elements which may be present in water without rendering it unsafe for domestic use. None of these substances are themselves poisonous or injurious in the amounts found in water. The amount present can merely be used as evidence of more or less recent contamination of the water with sewage. *A knowledge of the condition of the water before contamination is the best possible basis for a judgment.* On comparing the analysis of a water which is suspected to have produced disease with the analysis of the same water before the disease appeared, if a marked increase in the amount of chlorides or nitrogen is shown, contamination of the water may be suspected, and its source should be looked for by examining the watercourse from which the supply is drawn.

In cities where the water is analyzed at regular intervals and where a careful record of the cases of typhoid and other diseases known to be due to impure water is kept the amount of nitrogen, chlorides, etc., in the water which indicates a contaminated water-supply is soon learned.

652. Normal Chlorine.—These difficulties in interpretation arise from the fact that the substances introduced into the water with sewage also find their way into the water from sources which cannot produce dangerous contamination. While, for instance, the chlorides present in water may be due to sewage contamination, which always contains large amounts of chlorides, their presence is by no means *prima facie* evidence of such contamination. As the earth contains many salt deposits with which the water may come in contact, and the salt from the ocean undoubtedly diffuses through the earth for considerable distances inland, natural waters may contain large amounts of chlorides derived from these sources. The amount of chlorides derived from these sources by the water of a given region is known as the *normal chlorine* for the region. Maps have been prepared for many states giving isochlors, or lines passing through regions of equal chlorine. When the amount of chlorine found is in excess of the normal chlorine, contamination of the water with sewage is indicated.

653. Nitrogen.—As has been already stated, the ALBUMINOID AMMONIA may be derived from vegetable as well as from animal sources. A surface-water which has passed through a swampy region almost always contains a large amount of albuminoid ammonia. The presence of dissolved vegetable matter is almost always indicated by the high color of the water. On the other hand, the presence of much albuminoid ammonia in a light-colored water is almost always suspicious, the absence of color making it probable that the organic matter is partly of animal origin. If the free ammonia and nitrites are also high, the evidence of pollution is strong.

654. The Characteristics of Polluted Surface-waters are given by Geo. C. Whipple as follows:

“They contain an excess of chlorine above the normal of the region.

“They contain considerable organic matter, shown by the albuminoid ammonia and loss on ignition; but it should be remembered that the dissolved albuminoid ammonia may be explained by a high color.

“They contain free ammonia and nitrites, if the pollution is recent and the organic matter is in a decomposing state.

“They show coincident high nitrates and high hardness.

“They are characterized usually by a mouldy or musty odor and, if much polluted, by turbidity and sediment.”

655. Ground-waters are very different from surface-waters. As a rule they are clear, almost colorless, and without odor. Having been much in contact with the soil, they are rich in mineral matter. The fixed solids are higher, and usually the hardness. The amount of chlorine and nitrogen may be high, indicating pollution, but if the nitrogen is nearly all present as nitrate, the water has been purified by filtration through the soil and oxidation of the organic matter so that it may be safely used.

The determination of the amount of **TOTAL SOLIDS** as well as **HARDNESS** is carried out not so much to determine the sanitary character of the water as its suitability for laundry purposes, though the continued drinking of hard water is undoubtedly injurious to many constitutions. The presence of considerable amounts of iron renders water unfit for laundry use, the presence of more than 0.5 part per million being objectionable. If the water contains much organic matter, more iron may be present without being objectionable. A hardness of 25 to 50 is most desirable for ordinary use. A water of hardness of 50 is noticeably hard, while if above 100 it is classed as very hard.

The **COLOR** of water should not exceed 25. The amount of color which this figure implies may be judged from the fact that if the color of a water is 15 to 20 it will be noticed when the water is allowed to flow into a bath-tub, while if the color is 30 it may be noticed in a tumblerful.

Waters having a **TURBIDITY** of more than 3 or 4 are objectionable.

ANALYSIS OF WATER FOR USE IN BOILERS.

Aside from the sanitary analysis of water, the most commonly conducted analysis is that carried out for the purpose of determining the adaptability of the water in question to use in boilers. The water may not be suitable for use in boilers for two reasons.

It may, in the first place, contain substances which cause the **CORROSION** of the iron of which the boiler is made. **FREE ACIDS**, **MAGNESIUM CHLORIDE**, **AMMONIUM SALTS**, **MUCH DISSOLVED OXYGEN**, **HUMUS**, AND **FATTY SUBSTANCES** are the commonly occurring substances which have been found to cause corrosion in boilers.

A water may also be objectionable for boiler use from containing SCALE-FORMING INGREDIENTS, among which the most important are CALCIUM SULPHATE and CARBONATE and MAGNESIUM CARBONATE. Others occurring commonly, though in smaller amounts, are SILICA and the OXIDES OF IRON AND ALUMINIUM. Although rarely forming parts of the boiler-scale, the alkalis should in a careful analysis be determined, as the distribution of the hydrochloric and sulphuric acids present may then be more correctly determined.

656. Hardness.—The fitness of a water for boiler use may be somewhat roughly determined by simply determining the temporary and permanent hardness, as given in Chapter XXI, page 269. All of the calcium and magnesium carbonates constituting temporary hardness are precipitated by boiling and become part of the boiler-scale. The calcium and magnesium existing as permanent hardness may be present as chlorides or sulphates. The determination of permanent hardness does not give the amount of magnesium chloride present which causes corrosion, nor the amount of calcium sulphate present which is precipitated at the temperature existing in the boiler and constitutes part of the boiler-scale.

657. For a Complete Analysis an amount of water should be taken which will give from $\frac{1}{2}$ to 1 gram of residue. It is evaporated to dryness in a platinum dish and the TOTAL SOLIDS determined as already directed. The ignition of the residue to volatilize organic matter and burn the carbon must be conducted at dull redness and the ignition continued only for a few minutes, or a loss of alkalis may occur. After weighing, the residue is digested with water and a few cubic centimeters of hydrochloric acid. The insoluble residue is filtered off, washed, ignited in the platinum dish and weighed. It is mainly SILICA, though a little iron, aluminium, and calcium sulphate may be present. The silica may be volatilized by treatment with hydrofluoric acid and a drop or two of sulphuric acid, the residue weighed after ignition, and the weight deducted from that of the impure silica. The residue in the dish is dissolved by digestion with a little hydrochloric acid and water and is added to the main solution.

The IRON and ALUMINIUM may be precipitated with ammonia and weighed as oxides in the usual manner.

The CALCIUM is precipitated as oxalate from the filtrate and weighed as oxide.

The MAGNESIUM and the ALKALIES in the filtrate may be weighed together as sulphates, the solution being evaporated to dryness in a platinum dish and the ammonium salts volatilized after the addition of a few drops of sulphuric acid. A small amount of silica and other insoluble matter generally remains with the sulphates of magnesium and the alkalies. This is separated by treating the residue in the dish with water and filtering. The filtrate is again evaporated to dryness in the dish, and after gentle ignition is weighed. The weighed sulphates are dissolved in water, the solution diluted to 100 c.c. and divided into two portions, in one of which the magnesium is determined in the usual manner as pyrophosphate, while in the other portion the potassium is precipitated as platinochloride, washed according to the Lindo-Gladding method and weighed. The amount of magnesium present as sulphate is calculated from the weight of the pyrophosphate, and the weight of potassium as sulphate is calculated from the weight of the potassium platinochloride. The difference between the sum of these two weights and the weight of the combined magnesium and alkali sulphates gives the weight of sodium sulphate present.

The amount of CHLORIDES present is determined volumetrically according to the method given under the sanitary analysis of water on p. 421. The amount of SULPHATES present is also determined in a separate portion. Unless a considerable amount is present, 500 c.c. are evaporated down to a bulk of about 100 c.c. and, after acidifying with a drop or two of hydrochloric acid, the sulphuric acid is precipitated by the addition of barium chloride solution. After digestion on the water-bath the barium sulphate is filtered off, washed with hot water, ignited, and weighed in the usual manner.

If FREE MINERAL ACIDS are present, the amount is determined volumetrically by titration with a standard alkali.

658. Method of Combining Acids and Bases.—The elements present in the water having been determined, it remains to com-

bine them in such a manner that the properties of the water when used in a boiler may be easily shown, no attempt being made to combine them as they are believed to exist when in solution. The following method is generally followed: The chlorine is combined with the bases in the following order: sodium, potassium, magnesium, and calcium. The sulphuric acid is combined with the alkalies if the amount of chlorine was insufficient, then with the calcium and, if any remains, with the magnesium. The calcium and magnesium remaining are calculated as carbonates.

That this method of combination does not exist in solution is evident from the consideration that the strong base calcium would undoubtedly be in combination with some of the hydrochloric acid, while the alkalies would also be combined partly with the sulphuric and partly with the hydrochloric acid. When, however, the temperature was reached at which the calcium sulphate is almost absolutely insoluble in water this salt would be precipitated, even if the sulphuric acid were combined with the alkalies and the calcium with the hydrochloric acid. The ultimate result would therefore be that the alkalies would be found in combination with the chlorine, and the calcium with the sulphuric acid. Some authorities recommend that as much magnesium chloride as can be formed from the amounts of these elements present be reported in order to bring out the fact that the presence of the two elements together leads to the formation of hydrochloric acid and magnesium oxide. This method of reporting the analysis probably overstates the danger, as some of the magnesium is undoubtedly precipitated as carbonate if that acid is present in the solution.

659. Calculation of Results.—The simplest way in which to state the results is in grams per liter or in milligrams per liter, which would be identical with parts per million. The results must frequently be given in grains per United States gallon (58,318 grains) or per imperial gallon (70,000 grains), to suit the convenience of engineers who still use the English instead of the metric system.

The method of calculation may be more clearly understood from the following example. The analysis gave the following results:

SiO ₂	0.0063	gram per liter
SO ₃	0.0245	“ “ “
Cl.	0.0075	“ “ “
K ₂ O	0.0021	“ “ “
Na ₂ O	0.0065	“ “ “
MgO	0.0125	“ “ “
CaO	0.0223	“ “ “
Fe ₂ O ₃ + Al ₂ O ₃	0.0040	“ “ “

The sodium is first calculated to sodium chloride as follows:

$$\begin{aligned}\text{Na}_2\text{O} : 2\text{NaCl} &:: 0.0065 : x \\ 62 : 117.9 &:: 0.0065 : x \\ x &= 0.0123 \text{ gram NaCl.}\end{aligned}$$

The amount of chlorine in this weight of sodium chloride is then calculated:

$$\begin{aligned}\text{NaCl} : \text{Cl} &:: 0.0123 : x \\ 58.5 : 35.45 &:: 0.0123 : x \\ x &= 0.0075 \text{ gram Cl.}\end{aligned}$$

As this is the amount of chlorine found by analysis, no other chlorides are present.

The potassium is next calculated to sulphate:

$$\begin{aligned}\text{K}_2\text{O} : \text{K}_2\text{SO}_4 &:: 0.0021 : x \\ 94.3 : 174.36 &:: 0.0021 : x \\ x &= 0.0039 \text{ gram K}_2\text{SO}_4 \\ \text{K}_2\text{O} &= 0.0021 \quad \text{“} \\ \text{SO}_3 &= 0.0018 \quad \text{“}\end{aligned}$$

The amount of potassium oxide being subtracted, it is found that 0.0018 gram of sulphur trioxide has been taken to combine with the potassium, leaving 0.0227 gram (0.0245 - 0.0018) which is combined with calcium oxide to form sulphate.

$$\begin{aligned}\text{SO}_3 : \text{CaSO}_4 &:: 0.0227 : x \\ 80 : 136.2 &:: 0.0227 : x \\ x &= 0.0386 \text{ gram CaSO}_4 \\ \text{SO}_3 &= 0.0227 \quad \text{“} \\ \text{CaO} &= 0.0159 \quad \text{“}\end{aligned}$$

0.0064 gram (0.0223 - 0.0159) of calcium oxide remains after all of the sulphur trioxide has been combined to form sulphate. This calcium oxide will be present as carbonate.

$$\begin{aligned}\text{CaO} \cdot \text{CaCO}_3 &:: 0.0064 : x \\ 56 : 100 &:: 0.0064 : x \\ x &= 0.0114 \text{ gram of } \text{CaCO}_3.\end{aligned}$$

The chlorine and sulphur trioxide being all combined, all of the magnesium will be present as carbonate.

$$\begin{aligned}\text{MgO} : \text{MgCO}_3 &:: 0.0125 : x \\ 40.3 : 84.3 &:: 0.0125 : x \\ x &= 0.0261 \text{ gram } \text{MgCO}_3.\end{aligned}$$

The result of the analysis is therefore reported as follows:

$$\begin{aligned}\text{NaCl} &= 0.0123 \text{ gram per liter} \\ \text{K}_2\text{SO}_4 &= 0.0039 \quad " \quad " \quad " \\ \text{CaSO}_4 &= 0.0386 \quad " \quad " \quad " \\ \text{CaCO}_3 &= 0.0114 \quad " \quad " \quad " \\ \text{MgCO}_3 &= 0.0261 \quad " \quad " \quad " \\ \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 &= 0.0040 \quad " \quad " \quad " \\ \text{SiO}_2 &= 0.0063 \quad " \quad " \quad "\end{aligned}$$

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CHAPTER XXX.

ANALYSIS OF FATS AND OILS.

660. The Quantitative Analysis of a fat or oil is conducted for the purpose of identifying the constituent fats or oils as well as ascertaining the proportion in which they are present. The difficulties of the subject arise from the fact that not only are most pure fats and oils mixtures of a considerable number of chemical substances, but a given fat or oil, being produced as a part of an animal or vegetable structure, is by no means uniform in composition, but varies with the conditions under which it was produced. Changes in climate, season, food, etc., produce considerable variations in the fat or oil produced. The number of oils and fats which are produced on a commercial scale is very large, thus adding very much to the complexity of the subject. The mineral oils, being obtained by distillation of crude products from various parts of the earth, differ still more widely in composition. The strictly chemical examination is confined almost exclusively to vegetable fats and oils. The methods employed are essentially inorganic, and therefore come within the scope of this work. The interpretation of the results should be undertaken only after the consultation of a more extensive work on the subject,* except in the case of pure oils and comparatively simple mixtures.

661. Chemical Composition.—All animal and vegetable oils and fats are organic salts or esters in which a common base, GLYCERINE, is always present. Besides glycerine, most fats and oils and especially the waxes contain a larger or smaller quantity of a base peculiar to themselves. Of these, Benedikt and Ulzer

* A very excellent work for this purpose is that by Lewkowitsch on "Chemical Analysis of Oils, Fats, and Waxes." (Macmillan & Co.) A recent German publication is also excellent, "Analyse der Fette und Wachsarten." Benedikt und Ulzer. (Julius Springer, Berlin.)

mention twelve. Three of these belonging to the aromatic series furnish a means of distinguishing between fats and oils of vegetable or animal origin. CHOLESTERIN and ISOCHOLESTERIN occur exclusively in substances of animal origin, while vegetable products contain another base called PHYTOSTERIN. These may be liberated from the fatty acids by saponification, and after extraction with ether, may be crystallized from alcohol, cholesterol and isocholesterol forming irregular plates or tables, phytosterin, groups of needles. The first melts at 147° , the second at 138° , and the third at 132° – 134° . Failure to obtain these substances, however, is no indication that the oil or fat was not derived from its proper source, since they often exist in such small quantity as to be isolated with difficulty. The organic acids present in combination with the glycerine are very numerous and differ greatly in their properties. On these differences are founded most of the methods of identifying the oils and fats.

662. Acidity.—In many oils and fats, especially those of vegetable origin, part of the acid exists uncombined with the base. The amount of this free acid increases with the age of the oil, this being especially true of palm-oil. The amount of the free acid in most fresh animal oils is generally so small as to be negligible. Old and rancid fats become strongly acid.

The method of determining this value, as well as preparing the solutions required, is given in the following paragraphs.

663. Standard N/2 Hydrochloric Acid Solution.—Prepare 2 liters of a half-normal solution of hydrochloric acid by measuring out about 40 c.c. concentrated acid and diluting to a liter. Repeat the operation and pour the two solutions together and mix thoroughly. Standardize the solution by one of the methods given in Chapter XXI, page 258, and dilute to exact strength.

664. Standard N/2 Caustic Potash Solution.—Prepare some pure alcohol by adding to about 2 liters of the ordinary alcohol a few pieces of caustic potash, shaking thoroughly, and after allowing the solution to stand for a few hours, distilling off the alcohol. To 1 liter of the alcohol add 30 grams of caustic potash. The alcohol should be poured into a liter bottle, the potash added, and the bottle closed with a rubber stopper. Shake until the caustic potash is dissolved. The potassium carbonate will not dissolve, but

will adhere quite firmly to the sides and bottom of the bottle if the solution is allowed to stand undisturbed for a few hours. Decant or siphon off the clear liquid into another liter bottle, exposing the solution to the air as little as possible.

The solution is standardized by titrating with the standard hydrochloric acid, using phenolphthalein as the indicator. It should be protected from the carbon dioxide of the air both when being withdrawn from the bottle and during a titration. A simple method of accomplishing this object is to arrange a siphon for withdrawing the solution from the bottle, as shown in Fig. 50, p. 290. The siphon should be passed through a rubber stopper with two holes, a straight tube containing soda-lime being inserted in the second hole of the stopper. The end of the siphon exposed to the air should be kept closed with a piece of rubber tubing having one end closed with a glass plug. After being filled, the burette should be immediately closed with a small rubber stopper through which passes a soda-lime tube.

665. Determination of Free Acid.—For the determination of the acid value of oils, calculate the volume of the $N/2$ caustic potash solution to measure out and dilute with alcohol to 250 c.c. to make a fifth-normal solution. As the solution is not stable it must be used very soon after being made. All solid fats must be melted at as low a temperature as possible, and after standing until the impurities have settled, the clear fat is carefully decanted through a dry filter-paper. The vessel containing the oil or fat is weighed together with a small glass rod or spoon. From 1 to 2 grams are transferred to an Erlenmeyer flask, the exact amount being obtained by difference. 50 c.c. of the redistilled alcohol are now added and the flask shaken until the oil is dissolved. If the fat does not readily dissolve in alcohol, 50 c.c. of a mixture of equal parts of alcohol and ether may be used. One drop of phenolphthalein is now added. The solution is titrated with the fifth-normal caustic potash solution, which should be added drop by drop with constant and vigorous shaking. The first appearance of pink color is taken as the end-point. It may fade on standing a few minutes, but this is due to saponification of the neutral glycerides by the excess of alkali.

When oils of high free acid value, such as palm-oil or old and rancid fats are being tested, less than 1 gram may be taken for a

titration. When the acid value is small, as in most solid fats, as much as 5 or 10 grams may be taken to obtain a reliable determination. The number of milligrams of KOH per gram of fat or oil is calculated, which is the acid value. The acid value is also frequently expressed in terms of the amount of oleic acid corresponding to the amount of alkali used. The molecular weight of oleic acid being 282, 1 c.c. of N/5 alkali is equal to 0.0564 gram of oleic acid.

666. Köttstorfer Value.—As the acids present in fats and oils differ in molecular weight and basicity, varying amounts of alkali will be required to neutralize the acid in a definite amount of the oil or fat. Caustic potash is the alkali invariably used, 1 gram of the fat or oil being taken for the determination. *The so-called Köttstorfer value is the number of milligrams of KOH required to neutralize the acids present in 1 gram of the fat or oil.* When an oil or fat is treated with an alcoholic solution of caustic potash the union between the glycerine and the fatty acids is broken, so that the acid is left in combination with the potassium. This process is called SAPONIFICATION. An excess of standard caustic potash dissolved in alcohol is added to a weighed amount of the fat or oil. When the saponification is complete the excess of alkali is titrated with standard acid. The number of milligrams of KOH neutralized by one gram of the fat or oil is then calculated to find the Köttstorfer value.

667. Determination of Köttstorfer Value.—To determine the Köttstorfer or saponification value, weigh out as directed for the determination of free acid from 1 to 2 grams of the fat or oil into a small Erlenmeyer flask fitted with a cork to a return condenser. Add 25 c.c. of the alcoholic caustic potash solution with a pipette or a burette, and heat on the water-bath until the oil or fat is dissolved, which will require from ten minutes to half an hour, depending on the fat or oil being investigated. Measure out 25 c.c. of the caustic potash solution into a similar flask connected with a return condenser, and digest on the water-bath for the same time. Cool for a few minutes and titrate the contents of each flask with the N/5 hydrochloric acid, using rather more phenolphthalein than usual as the indicator. The difference between the acid used in the two titrations gives the acid necessary to neutralize the alkali

used in the saponification. Calculate the number of milligrams of KOH necessary to saponify 1 gram of the fat or oil.

668. Ether Value.—The ether value is the difference between the saponification and the acid value.

669. Reichert and Reichert-Meissl Value.—Some of the fatty acids of small molecular weight are quite volatile, and also soluble in water. It has been found that by liberating the acids contained in a given fat or oil, adding water, and distilling off this water again, a distillate is obtained which contains a considerable percentage of the volatile acids. It is found in practice that the total amount of volatile acid present is not separated in this manner by one distillation. *The amount which comes over depends upon the dilution of the solution, the amount of the distillate, and the rapidity of the distillation.* The amount of acid in the distillate is determined by titration with decinormal caustic potash. The REICHERT VALUE indicates the number of cubic centimeters of N/10 potash required to neutralize the acid from 2.5 grams of fat contained in 100 c.c. of distillate, 110 c.c. of which has passed over in one-half hour. The REICHERT-MEISSEL value is obtained in the same manner, 5 grams of fat having been used instead of 2.5 grams. This number is not necessarily twice the Reichert number. This determination has been used more especially to distinguish butter from the artificial substitutes which have been put on the market.

670. Determination of Reichert-Meissl Value.—For the determination of the Reichert-Meissl number a sample of butter-fat should be used which has been freed from casein, water, salt, etc., by melting and filtering as already directed. A quantity of this fat as nearly as possible 5 grams is weighed out into a 250-c.c. Erlenmeyer flask, 2 c.c. water, 8 c.c. alcohol, and a stick of caustic soda weighing about 2 grams are added. Attach the flask to an inverted condenser by means of a cork stopper and heat on the water-bath for one hour, shaking the contents of the flask occasionally. Remove or incline the condenser and distil off the alcohol by immersing the flask in the hot water and heating for about three-quarters of an hour. After the alcohol is removed add 100 c.c. recently boiled distilled water and dissolve the soap by warming on the water-bath and shaking. Cool the solution to

60° or 70° and add 50 c.c. of a solution of sulphuric acid containing 25 c.c. concentrated acid per liter. Again attach the flask to the inverted condenser and heat on the water-bath until the insoluble acids collect in a clear oily layer on top of the liquid. Allow the contents of the flask to cool to the room temperature. Introduce a few pieces of pumice-stone which have been heated to redness and dropped into distilled water. Attach the flask to an inclined condenser and distil off 110 c.c. into a graduated cylinder, regulating the heat so that thirty minutes as nearly as possible shall be required for the distillation. Mix the distillate thoroughly by pouring back and forth into a dry beaker. Filter through a dry paper into a 100-c.c. flask. Pour into a beaker, add a few drops of phenolphthalein, and titrate with N/10 alcoholic KOH made by diluting the half-normal solution. When the end-point is reached the 100-c.c. flask is rinsed and the titration completed. The number of cubic centimeters of N/10 alkali used multiplied by 1.1 gives the Reichert-Meissl number.

671. The Polenske Value.—This method of examining butter-fat has come into use for the detection of cocoanut-oil, which has been largely used for the adulteration of butter. The Reichert-Meissl value has been generally relied on to detect the admixture of foreign fats in butter, on account of its high value in the case of butter-fat and the low value given by other fats, except cocoanut-oil, which gives a Reichert-Meissl value of 7 to 7.8, so that a considerable amount of this oil can be mixed with a butter having a high value, 30 for instance, producing a mixture which would have a Reichert-Meissl value above the legal limit of 20 to 24. Polenske found that the greater part of the volatile fatty acids of butter obtained in the Reichert-Meissl determination are soluble in water, while the reverse is true of cocoanut-oil. The amount of the soluble and insoluble acids is obtained, as in the Reichert-Meissl determination, by titration with decinormal caustic potash, and the values are given in cubic centimeters of the alkali. For butter-fat the insoluble volatile fatty acids required 1.5 to 3.0 c.c. of the decinormal alkalies, while 16.8 to 17.8 c.c. was required for the insoluble volatile fatty acids from cocoanut-oil. The Polenske value varies with the Reichert-Meissl value, as is shown in the table on page 459.

672. The Determination of the Polenske Value is made in a manner very similar to the Reichert-Meissl determination. It has been found that the details of the method must be adhered to very strictly in order to obtain concordant results. Five grams of the butter-fat are placed in a 300-c.c. flask and saponified with caustic soda and glycerine. For this purpose 2 c.c. of a caustic-soda solution, prepared from equal parts of caustic soda and water, and 20 grams of glycerine, are added, and the flask heated over the free flame until saponification is complete. The solution is allowed to cool below 100° , and 90 c.c. of water added. The mass is dissolved by warming on the water-bath to 50° C. The solution must be clear and colorless. If it is brown it has been overheated during the saponification and must be rejected and the saponification repeated. 50 c.c. of dilute sulphuric-acid solution containing 25 c.c. concentrated sulphuric acid per liter are now added, and the volatile acids distilled off. For this purpose $\frac{1}{2}$ gram of pumice is added. This pumice must be broken and sifted so as to include only pieces of 0.5 to 1 mm. diameter. The flask is placed on copper or brass gauze of 0.5 mm. mesh. The flask is connected to an upright condenser by means of a bulb tube. The bulb is immediately above the stopper of the flask, and the tube passing to the condenser is inclined toward the bulb, which must be 70 mm. from the condenser. The heat is regulated so that 110 c.c. are distilled off in 19 to 20 minutes. The cooling water must flow rapidly enough through the condenser to cool the distillate to 20° – 23° C. as it drops into a 110-c.c. flask, which serves as a receiver. When 110 c.c. have distilled over, the flask is replaced with a 20-c.c. measuring cylinder.

The 110-c.c. flask containing the distillate is immersed, without shaking, in water at 15° C. After about 5 minutes the neck of the flask is tapped lightly, so as to cause the drops of oil floating on the surface of the liquid to adhere to the walls of the flask. After another 10 minutes the consistency of the oily drops is noted. If the butter is pure and has a high Reichert-Meissl value, the drops will be semi-solid and milky. If the Reichert-Meissl value is low, or 10 per cent or more of cocoanut-oil is present, the insoluble fatty acids do not solidify, but remain clear and oily. The contents of the flask are mixed by inverting it

several times without violent shaking, and 100 c.c. filtered through an 8-cm. filter-paper and titrated with tenth-normal caustic potash. The insoluble acids on the paper are washed free from soluble acids by washing with three 15-c.c. portions of water which have been passed through the condenser tube and the 20-c.c. cylinder and the 110-c.c. flask. The insoluble acids are then dissolved in neutral 90 per cent alcohol by passing three 15-c.c. portions through the condenser tube, the 20-c.c. measuring cylinder, the 110-c.c. flask, and the filter-paper. Each portion is allowed to drain completely before adding a fresh portion. The combined alcoholic solution is then titrated with tenth-normal alkali to obtain the Polenske value.

673. The Hehner Value is the converse of the Reichert value, the percentage of insoluble acids being determined by saponifying the fat, adding an excess of mineral acid so as to liberate the fatty acids, then filtering off, washing, and weighing the insoluble portion.

674. The Iodine Value of oils and fats is obtained by allowing a measured amount of an iodine solution to act on the oil or fat. It has been found that a considerable amount of the halogen is absorbed by the fatty acids present. The percentage of the halogen absorbed is taken as the iodine value. The chemical reactions which take place are not fully understood. In general it is thought that in the unsaturated acids the double bond is broken and the iodine enters at this point into the molecule. There seems to be no doubt, however, that substitution takes place to a limited extent, an atom of iodine taking the place of an atom of hydrogen, which unites with another atom of iodine, forming hydriodic acid. Solutions of bromine have been used in the same manner, while recently solutions of iodine monochloride and also solutions of iodine monobromide have come into use. The results are almost universally computed as percentage of iodine absorbed. Slightly different values are obtained by the use of these different solutions. Strictly comparable results can be obtained only by working with the same solutions and under the same conditions, especially as to the time during which the halogen is allowed to act on the oil or fat.

675. Wijs' Iodine Monochloride Solution.—For the determination of the iodine, the Wijs solution of iodine is the most

advantageous for use. This is a solution of iodine monochloride in glacial acetic acid. The acid must be the strongest and purest obtainable, giving no reduction with sulphuric acid and potassium dichromate. The percentage of acid must not be less than 99 and can be most readily determined by taking the melting-point which varies with the amount of water present, as is evident from the following table:

Per cent of $\text{H.C}_2\text{H}_3\text{O}_2$.	Melting-point.
100	16.75
99.5	15.65
99	14.80
97.09	11.95
95.24	9.40

The test is made by half filling an 8-inch test-tube with the acetic acid. This test-tube is suspended within a larger test-tube by means of a cork, through which the smaller tube is passed. A delicate and accurate thermometer is placed in the acid, which is cooled by immersing the whole in ice-water. As soon as the acetic acid begins to crystallize, the temperature rapidly rises to the true melting-point of the acid. The advantage of using this solution is that its titre remains unchanged for months, and the time necessary for a determination is reduced from four or six hours to a few minutes.

Thirteen grams of pure iodine is dissolved in a liter of the acid. The exact strength is then determined by titration against a standard thiosulphate solution. Chlorine free from hydrochloric acid is passed into the solution until the dark-brown color changes to a light-brown or yellow color. The strength should then be determined again by titration against the thiosulphate solution, and should be double the original strength. It is advisable, however, to have a slight excess of iodine present rather than of chlorine.

676. Hanus' Monobromide Solution.—The Hanus solution serves the same purpose as the Wijs solution, and is more easily made. Instead of passing chlorine into the acetic-acid solution of iodine, liquid bromine is added until the titre is doubled. About 3.0 c.c. will be found sufficient.

677. Sodium-thiosulphate Solution.—An N/10 sodium-thiosulphate solution is made up and standardized by means of re-sublimed iodine. This solution is then titrated against the iodine solution. For this purpose 20 c.c. of the iodine solution are measured out into a beaker, 100 c.c. distilled water added, and 1 gram potassium iodide dissolved in 10 c.c. water. The thiosulphate solution is then added until a faint yellow color is obtained, the starch solution is added, and the titration completed.

678. Determination of Iodine Value.—To determine the iodine value of an oil, from 0.15 to 0.2 gram of a drying-oil, 0.3 to 0.5 gram of a non-drying oil, or 0.7 to 1 gram of a solid fat is weighed out and transferred to a glass-stoppered bottle. The most convenient method of weighing out oils is to pour a suitable amount into a small beaker, place in the beaker a short glass tube, and weigh carefully. By means of the glass tube, drop some of the oil into the bottle, replace the tube in the beaker, and weigh again. The oil may also be weighed in a tared homeopathic shell vial. The vial containing the oil is introduced into the glass-stoppered bottle. The oil or fat is dissolved in 10 c.c. of chloroform and 25 to 50 c.c. of the iodine solution are added. The iodine must be present in excess. If the iodine solution is very much decolorized by the oil, more must be added. The iodine should be allowed to act for fifteen minutes for non-drying oils, thirty minutes for semi-drying oils, and one hour for drying oils. A blank determination is carried on at the same time, 10 c.c. of the chloroform being treated with iodine solution for the same length of time.

After the iodine has acted on the oil, 10 c.c. of a 10% solution of potassium iodide free from iodate are added to the bottle, and this is followed, after thorough agitation, by about 100 c.c. of distilled water, care being taken that all of the iodine solution is washed down from the stopper, neck, and walls of the bottle. The excess of iodine is then titrated with thiosulphate. The number of cubic centimeters of thiosulphate used, subtracted from the amount required for the blank, represents the amount of iodine absorbed by the oil. The equivalent weight of iodine thus found is divided by the weight of oil taken, and the result expressed in per cent as the iodine number.

679. Determination of Rosin in Shellac by A. C. Langmuir's Method.*—The iodine value of unbleached shellac varies from 15 to 18 per cent, while that of rosin varies from 175 to about 260. It is possible, therefore, to ascertain approximately the amount of rosin present in a given sample of shellac by a determination of the iodine number. For calculating the result, 18 is used as the iodine number of the shellac, and 228 as that of the rosin. By using these figures the percentage of the adulterant which is found may be slightly lower than that actually present. This is in accord with the accepted commercial principle that the inaccuracies in a method of analysis shall favor the seller rather than the buyer, by assigning the lowest possible value to the amount of impurities present. The calculation is made according to the formula

$$y = 100 \frac{A - M}{N - M},$$

where y = per cent of rosin;

M = iodine number of shellac;

N = " " " rosin;

A = " " " mixture.

Substituting the fixed values of M and N , the formula becomes

$$y = 100 \frac{A - 18}{210}.$$

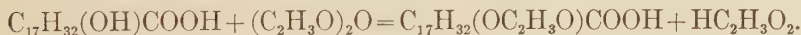
The iodine number is determined by means of the Wijs solution. Exactly 0.2 gram of the ground sample is introduced into a dry 250-c.c. glass-stoppered bottle. 20 c.c. of glacial acetic acid is introduced and warmed until the shellac is dissolved, with the possible exception of a little wax. 10 c.c. of chloroform is then added and the solution cooled to 21°–24° C. This temperature must be maintained during the remainder of the test. 20 c.c. of the Wijs solution is introduced by means of a pipette. The bottle is allowed to stand in water having a temperature of 22° to 23° for exactly 1 hour.

* Ber., 31, 750. J. Soc. Chem. Ind., 17, 609. Jour. Am. Chem. Soc., 29, 1221.

Pure shellac will scarcely alter the color of the Wijs solution. If rosin is present, a reddish-brown color will be produced, the depth of which depends on the amount of rosin present. After standing 1 hour, 10 c.c. of a 10 per cent potassium-iodide solution is added. The excess of iodine is immediately determined by means of a tenth-normal solution of sodium thiosulphate. When the iodine color is nearly gone, a little starch is added and the titration completed. Any color returning after a half-minute is disregarded.

On account of the large coefficient of expansion of the Wijs solution, a blank determination should be made with that of the shellac. The determination is carried out in exactly the same manner, with the exception of the addition of the shellac.

68o. Acetyl Value.—This permits the identification of *castor-oil*, *grapeseed-oil*, and of *oxidized fish oils* in mixtures. Besides this, many *fish oils* show a comparatively high acetyl value. The test is founded on the action of acetic anhydride upon alcoholic hydroxyls as they exist in the oxyacids, as is shown in the following reaction:



Upon saponification of the acetylated fatty acid thus produced, the hydroxyl is again replaced and the acetyl group liberated as an acetate. The amount of acetic acid liberated may be determined, giving the acetyl value. Benedikt first proposed this method, operating on the fatty acids, but the process was modified by Lewkowitsch, who works on the oils or fats directly, giving more exactly the true content of hydroxy acids.

681. Determination of Acetyl Value.—The method adopted by the Association of Official Agricultural Chemists is carried out as follows: Boil a portion of the oil or fat with an equal volume of acetic anhydride for two hours and pour the mixture into a large beaker containing 500 c.c. of water, and boil for half an hour. To prevent bumping, a slow current of carbon dioxide is passed into the liquid through a finely drawn-out tube, reaching nearly to the bottom. Allow the mixture to separate into two layers, siphon off the water, and boil the oily layer with fresh water until it is no longer acid to litmus-paper. The acetylated fat is then separated from the water, filtered, and dried in a drying-oven.

Weigh from 2 to 4 grams of the acetylated fats into a flask and saponify with alcoholic potash, as in the determination of the saponification number. If the distillation process is to be adopted it is not necessary to work with a standardized alcoholic-potash solution. In case the filtration method is used, which will be found much shorter, it is necessary that the alcoholic potash be measured exactly. In either case evaporate the alcohol after saponification and dissolve the soap in water. Now two procedures are possible, either distillation or filtration.

(a) DISTILLATION PROCESS.—Acidify with dilute sulphuric acid (1-10) and distil the liquid, as in the Reichert test. As several hundred cubic centimeters must be distilled, either a current of steam is run through or portions of water are added from time to time. From 500 to 700 c.c. of distillate will be found sufficient. Filter the distillates to remove any insoluble acids carried over by the steam, and titrate the filtrate with decinormal potassium hydroxide, using phenolphthalein as the indicator. Multiply the number of cubic centimeters of alkali employed by 5.61, and divide by the weight of substance taken. This gives the acetyl value, which is the number of milligrams of KOH required to neutralize the acetic acid liberated from one gram of the acetylated fatty acid.

(b) FILTRATION PROCESS.—Add to the soap solution a quantity of the standard sulphuric acid exactly corresponding to the amount of alcoholic potash added, warm gently, and the free fatty acids will collect on top. Filter off the liberated fatty acids, wash with boiling water until the washings are no longer acid, and titrate the filtrate with decinormal potassium hydroxide, using phenolphthalein as the indicator. Calculate the acetyl value as before.

PHYSICAL TESTS.

Besides the constants obtained by strictly chemical quantitative means, there are a few physical tests that are extremely important and widely used, which it seems advisable should be mentioned under the head of oil-analysis.

682. **Specific Gravity.**—This may be very accurately obtained by means of a Westphal balance as described on p. 275.

If the oil is viscous, however, a pycnometer must be used as described on p. 274.

683. Index of Refraction.—This is found by means of an instrument called a refractometer, of which there are several on the market. The Zeiss butyro-refractometer, one of the simplest of these, is also one of the most efficient. The oil or fat is introduced as a thin film between two halves of a Nicol's prism, which are enclosed in a hollow metal jacket through which water is allowed to flow, maintaining a constant temperature. The degree of diffraction is indicated on an arbitrary scale by a shadow which is observed through a telescope attached to the prism, and this reading, by comparison with a table, made especially for the instrument, is converted into the refractive index.

The Abbé refractometer is better suited for general use, being constructed with prisms and water-jackets like the Zeiss butyro-refractometer, but instead of an arbitrary scale fixed in the telescope, the border of a shadow, visible through the latter, is brought to the intersection of cross-hairs by moving an arm at the side of the instrument, and the refractive index may then be read directly on a scale along which the movable arm slides.

684. Maumene Number and Specific Temperature Reaction.—

It is found that by mixing various oils with concentrated sulphuric acid a reaction ensues, causing a rise of temperature in the mixture, which for the same oil under the same conditions and with the same concentration of acid is a constant. In order to bring more uniformity into the results obtained by different operators working under different conditions and using different strengths of acid, the old Maumene test has been modified with considerable success. Maumene mixed 50 grams of oil with 10 c.c. of concentrated acid in a small beaker sunk in a larger vessel filled with cotton or some other insulating material. Before mixing, both oil and acid were at the same temperature, as close to 20° as possible. This temperature was noted, and, after combining, the highest point registered by the thermometer used for stirring the mass was observed, which, minus the initial temperature, gave the Maumene number. The errors introduced by different degrees of insulation and strength of acid have been eliminated by conducting another test exactly as the one just

described, using the same apparatus and the same acid, but substituting 50 c.c. of pure water for the oil. Then, by the following formula:

$$S = \frac{100A}{B},$$

in which S = specific temperature number,

A = Maumene number,

B = rise of temperature obtained with pure water under the same conditions as those used in the Maumene test,

results are obtained which compare admirably, provided the acid used is fairly concentrated—between 95 and 99 per cent.*

685. The determination is carried out as follows:† A beaker, 5 inches by 1½ inches, is placed inside another, 6 inches by 3 inches, and a wet mixture of asbestos and plaster of Paris tightly packed around the inner one. This, when dried, makes a hard, solid packing which radiates heat very slowly.

Remove the inner beaker, weigh into it 50 grams of fat or oil, and note the temperature carefully. Then from a pipette which will deliver it in approximately one minute add 10 c.c. of 96–98% sulphuric acid, which is at the same temperature as the oil. While the acid is being introduced, stir the oil and acid with an accurate thermometer. Then hold the thermometer-bulb carefully in the centre of the mixture, and when the mercury reaches the highest point note the reading. It is easy to determine this point, as the column of mercury remains stationary for some time. It is necessary to take care not to read the temperature too soon, as some oils take considerable time to reach their maximum point. The difference between the initial reading and the final reading, expressed in degrees centigrade, gives the Maumene number.

In order to get the specific temperature number the operation is repeated with the same apparatus and the same acid, using 50 c.c. of pure water in place of the oil. It is advisable in this case to cover the beaker with a piece of cardboard or heavy paper

* References: *Journal Soc. Chem. Ind.*, 1 91, 10, 233; *Jour. Amer. Chem. Soc.*, 1902, 24, 266.

† Allen, *Com. Org. Anal.*, 3d Ed., Vol. II, Pt. 1, p. 76.

twice the diameter of the latter, the thermometer being thrust through a small hole in the centre. This interferes with the evaporation of the water and the consequent fall of the temperature of the mixture, but if employed should be used with the oils also.

686. Melting-point of Fatty Acids.—This test is much used in corroborating results obtained by other methods when the question of identity or purity of an oil or fat arises. The sample is saponified by boiling with an excess of alcoholic potash, and the fatty acids liberated, as in the Hehner method, with dilute sulphuric acid and washed with warm water until the washings show a neutral reaction. The melted fatty acids are then drawn into a very thin-walled capillary tube 1 or 2 inches long according to the length of the bulb of the thermometer used. The capillary is sealed about one-fourth inch above the filled portion by holding in the outer mantle of a Bunsen flame and drawing out when the glass softens. The tube thus prepared, after cooling in a refrigerator, is fastened to the bulb of the thermometer by an elastic band and immersed in a glycerine bath, which, to secure a slower and more even rise, may in turn be surrounded by a second bath of the same material which is directly heated by a Bunsen flame. By regulating the flame the rise of temperature may be readily controlled. A slow rotary motion is maintained by the thermometer with its capillary until the fatty acids become transparent, when the temperature is noted. It is almost always necessary to conduct three tests; the first to get the approximate temperature, after which the heating may be done very slowly as the melting-point approaches, and the average of the two last determinations taken as the true point.

687. Detection of Phytosterol and Cholesterol.—Fats and oils of vegetable origin may be detected in those derived from animals by the presence of phytosterol and, vice versa, animal products in vegetable oils and fats by the presence of cholesterol. Boil 50 grams of the fat or oil in a flask having a reflux condenser, with 75 c.c. of 95% alcohol, for five minutes, and separate the alcoholic solution. Repeat with another portion of alcohol and separate. Mix the alcoholic solution with 15 c.c. of 30% sodium hydroxide,

and boil in a flask with an air condenser until one-fourth of the alcohol is evaporated. Evaporate nearly to dryness in a porcelain dish and extract the residue with successive portions of ether. Evaporate the ethereal solution to dryness, take up with a little ether, filter, again evaporate, dissolve in hot 95% alcohol, and allow to crystallize. Examine a few of the crystals under a microscope. Phytosterol thus prepared appears as tufts of needles, cholesterol as thin rhombic tables. The melting-point of phytosterol is 130° – 137.5° , that of cholesterol 146° .

The melting-point is better determined, however, on the acetates of these alcohols. The crystals obtained as described are heated in a dish, with 2–3 c.c. of acetic anhydride, over a small flame until it boils, the dish being covered with a watch-glass. The watch-glass is then removed and the excess of acetic anhydride evaporated off on the water-bath. The contents of the dish are next heated with the smallest quantity of absolute alcohol, and in order to prevent immediate solidification or crystallization, a few c.c. of alcohol are added, and the mass allowed to crystallize by spontaneous evaporation of the alcohol, of which one-half or a third is allowed to volatilize. The crystals are filtered off through a small filter and washed with a little 95% alcohol. They are then dissolved in 5–10 c.c. of hot absolute alcohol and again allowed to crystallize. These crystals are filtered off, pressed dry, and their melting-point determined. Cholesteryl acetate melts at 114.3° to 114.8° (corr.), and phytosteryl acetate at 125.6° to 137° (corr.). In doubtful cases the crystals should be redissolved in hot absolute alcohol and recrystallized at least three times before obtaining the melting-point.

688. Flash Point.—This is the temperature at which the vapors given off by the oil may be ignited, producing a flash when brought in contact with a small flame. This test is made in order to determine the temperature at which the use of the oil involves the danger of fires or explosions. The flash point varies with the form of apparatus and the method of making the test, so that the conditions must be rigidly fixed in order to obtain constant results. Various forms of apparatus have been devised, all of which embody a few essential features, such as a cup to hold the oil, some device for gradually raising the temperature of the oil,

a thermometer to indicate the temperature, and a small flame to be used for igniting the vapor. A cover containing two openings, one for the thermometer and another at which to apply the test-flame, is sometimes provided. Such an instrument is called a closed tester, while an instrument without a cover is called an open tester. The open testers give higher readings than the closed testers. More accurate determinations can be made with the closed testers.

689. Oil Testers.—A simple tester may be made from ordinary laboratory apparatus. A shallow porcelain crucible of about 100 c.c. capacity will serve as the cup to contain the oil. It may be heated on a sand-bath, or it may be placed in a circular opening in a piece of asbestos board and heated over a Bunsen-burner flame. A thermometer is suspended in the oil, which is then slowly heated while a small test-flame is passed over the surface of the oil. The test-flame may be produced by drawing out a piece of glass tubing to a fine tube and attaching it to the gas-supply by means of rubber tubing. The temperature is noted at the moment a flash is produced. After the oil has cooled somewhat, the test is repeated, the oil being heated more slowly as the temperature approaches the point at which the oil flashes. By placing a metallic or glass cover containing two openings over the crucible, it can be used as a closed tester.

Tagliabue's tester is constructed entirely of copper and contains two cups. The large one serves as a receptacle for a non-volatile oil in which the smaller cup containing the oil to be tested is immersed. The heat is applied to the larger cup. By this device the temperature of the oil in the inner cup is raised more uniformly. In a similar form of tester known as the "Say-bolt," the test-flame is replaced by a spark of electricity produced by an induction-coil.

690. Viscosity is that property of a liquid which determines the relative rate of flow under fixed conditions. It is usually determined by noting the time required by a definite volume of oil at a definite temperature to flow through a small aperture. Water is usually taken as the standard. The simplest form of apparatus is that used in the Pennsylvania and other railroad laboratories. A 100-c.c. pipette, having a bulb 1.5 to 1.75 inches

in diameter and about $4\frac{1}{2}$ inches long, is graduated so that the 100-c.c. mark is just at the bottom of the bulb. The opening of the pipette is then made of such a size that 100 c.c. of water at 100° F. will run out of the pipette in 34 seconds. After drying the pipette, the oil to be tested is warmed to 100° and 100 c.c. is drawn up into the pipette. The time required for the oil to flow out is noted. This gives the viscosity of the oil. It is also becoming customary to take the ratio between the number of seconds required by the water and the oil as the viscosity.

A considerable number of instruments have been devised for this determination, Engler's, Tagliabue's, Redwood's, and Gibbs' being standard instruments. All of these instruments contain a cup having a small opening at the bottom, through which the oil is allowed to flow. A jacket is generally provided which can be filled with water or oil and heated, thus maintaining the oil at a constant temperature. The oil is delivered into a flask of known capacity.

691. Oil Analysis.—In the examination of an unknown oil or fat, the first test to be made is the determination as to whether the oil is of mineral or organic origin, or a mixture of these two classes of oils. For this purpose advantage is taken of the fact that organic fats and oils can be saponified, while mineral oils and waxes cannot be converted into a soap, but can be extracted with ether, while the soap produced from the organic fats and oils is insoluble in ether. On evaporating off the ether, the mineral oil can be recovered in pure condition. On acidifying the water solution of the soap, the fatty acids of the vegetable or animal oils separate out as an oily layer. As the fatty acids represent about 95% of most animal or vegetable oils, the weight of these acids can be used to calculate the amount of these constituents. A determination of the chemical and physical constants of the fatty acids can be made for the identification of the oils present. If mineral oils are absent, these determinations are made on the original oil.

692. The Saponification is carried out in the same manner as the determination of the Köttstorfer value (page 439). Standard solutions of the caustic potash and acid are not necessary.

60 grams of caustic potash are dissolved in one liter of 95% alcohol. 5 to 10 grams of the fat or oil to be tested are weighed out into an Erlenmeyer flask and 50 to 75 c.c. of the alcoholic caustic potash added. The flask is heated on the water-bath with a return condenser until the oil is saponified. 75 c.c. of water is then added and the heating continued without the condenser until the alcohol has been expelled. The soap solution is transferred to a separatory funnel and 75 c.c. of ether added. The funnel is corked and the contents thoroughly shaken and then allowed to stand quietly until the upper ether solution of the unsaponified or mineral fat is completely separated from the lower water solution of the soap formed from the animal or vegetable fat. The lower layer is drawn off into a beaker, the stop-cock being closed when the last drop of the water solution has passed out. A little ether may be allowed to pass out with the water solution, but none of the latter must be allowed to remain with the ether. The ethereal solution is drawn off into a small weighed flask and the water solution returned to the funnel and the extraction with ether repeated. Three or four extractions with ether are generally sufficient to remove all the unsaponified fat or oil. The last portions of ether should leave no residue when allowed to evaporate on a watch-crystal. The flask containing the ethereal solution is connected with an inclined condenser and the ether distilled off over a water-bath, or, still better, over an electric-light bulb. As the ether vapor is both inflammable and explosive when mixed with air, a flame should not be brought near vessels containing ether. The residue remaining after distilling off the ether is dried on the water-bath, or at a lower temperature if volatile oils are present and weighed. This gives the weight of mineral oil present.

693. Determination of the Fatty Acids.—The aqueous solution of the soap is acidified with hydrochloric acid and heated on the water-bath until the fatty acids form a clear layer on the water solution. The oily layer is filtered off on a wet filter-paper which has been dried for one hour in the steam-oven together with a small beaker and weighed. The oil is washed with hot water without allowing the funnel to become more than half empty. When the chlorides have been completely washed out, the paper

containing the fatty acids is transferred to the beaker which was weighed with the paper, and the whole placed in the steam-oven to dry. After one hour it is weighed and again dried and weighed until the weight is constant. In order to determine what organic oils are present in the sample being analyzed, a determination of the various constants of the fatty acids is made.

694. Identification of Oils.—For the identification of an unknown organic oil, the most useful constant is the iodine value, on account of the great difference in this value for various oils. When two or more oils have the same iodine value as given in the table, page 457, other constants must be determined. An iodine value of 103, for example, might indicate cottonseed, mustard, rape, or sesame oil. A saponification value of 193 would show that the oil must be cottonseed or sesame oil, while an acetyl value of 16.6 would indicate that the oil must be cottonseed. This conclusion could be confirmed by qualitative color tests, of which some very excellent ones are known.

IODINE VALUE OF OILS. *

	By Hübl's Solution.	By Wijs's Solution.	By Hanus' Solution.	Authority.
Butter.	35.3	36.2	35.3	Tolman and Munson
"	34.8	35.9	35.4	" " "
"	30.7		30.6	Hanus
"	19.5 to 38.9			
Cocoanut.	8.93	9.05	8.60	Tolman and Munson
"	9.03		9.03	Hanus
"	8 to 9.5			
Corn.	119.0	123.2	120.2	Tolman and Munson
"	119.0	122.2	119.6	" " "
"	123.3	129.2	126.0	" " "
"	124.8	128.4		Wijs
"	111.2 to 122.9			
Cottonseed-oil. . .	103.8	105.3	105.2	Tolman and Munson
"	106.2	107.3	107.8	" " "
"	104.8	106.2	106.7	" " "
"	100.9 to 116.9			
Konut.	6.09	6.43	6.40	" " "
Lard-oil.	73.7	74.5	73.9	" " "
"	69.3	70.5	69.8	" " "
"	56.4		56.9	Hanus
"	50.4 to 77.28			
	(Decreases to 22	with age)		
Linseed-oil.	169.8	186.5	184.5	Tolman and Munson
"	179.5	188.7	183.7	" " "
"	174.8	177.3	174.5	Hunt
"	180.9	182.1		Wijs
"	170.2		171.0	Hanus
"	171 to 188			
Magnolia-oil. . . .	81.7	79.4	78.9	Tolman and Munson
"	76.1	75.6	74.0	" " "
Mustard-oil.	110.4	118.5	115.5	" " "
"	113.0	118.2	116.8	" " "
"	98.4	104.3	103.8	" " "
"	103.5	112.5	110.2	" " "
"	106.4	117.3	114.8	" " "
"	92.1 to 106.57			
Oleo-oil.	42.6	43.5	43.3	" " "
Oleomargarine . . .	53.6	53.5	52.3	" " "
"	52.8	53.7	52.2	" " "

IODINE VALUE OF OILS*—*Continued.*

	By Hübl's Solution.	By Wijs's Solution.	By Hanus' Solution.	Authority.
Oleomargarine.....	52.5	52.9	52.0	Tolman and Munson
"	66.3	66.0	64.8	" " "
Olive-oil.	79.2	79.9	80.6	" " "
"	80.5	80.9	81.6	" " "
"	84.8	86.7	86.5	" " "
"	89.8	91.4	90.0	" " "
" av. 36 samples.	84.1	85.3	84.7	
"	77.28 to 91.5			
Peanut- or Arachis-oil	96.3	99.0	97.4	Tolman and Munson
" " "	94.5	95.2	94.1	" " "
" " "	88.3		88.4	Hanus
" " "	87.2	87.2		Wijs
" " "	91.8	93.4	91.6	Hanus
" " "	85.6 to 105			
Poppy.....	133.4	135.2	132.9	" " "
"	134.9	139.1	138.4	" " "
"	122.4		122.6	Hanus
"	134.6		135.2	"
"	119.6	119.6		Wijs
"	132.6 to 143.3			
Rape	101.3	105.7	105.2	Tolman and Munson
"	100.2	104.1	102.8	" " "
"	99.3		98.8	Hanus
"	102.9	103.3		Wijs
"	103.0	102.1	101.9	Hunt
"	97 to 106			
Sesame.....	106.4	107.0	106.5	Tolman and Munson
"	110.3	111.7		Wijs
"	107.1		107.5	Hanus
"	102.7 to 112			
Sunflower	106.4	109.2	107.7	Tolman and Munson
"	117.8	119.0		Wijs
"	119.7 to 135			

* For other iodine values and other constants, see Van Nostrand's Chemical Annual.

REICHERT-MEISSEL-VALUE.

	c.c. N/10 KOH.		c.c. N/10 KOH.
Butter.....	19.8-33.5	Cocoanut-oil *.....	7.0-7.8
Legal minimum in Great Britain, Germany, and France.....	24.0	Margarine.....	2.6
Legal minimum in Sweden... ..	23.0	Oleomargarine.....	0.8-0.9
“ “ Italy.....	20.0	Palm-oil.....	5.0
Rabbit-fat.....	5.6	Wool-fat.....	8.0
		Beef-marrow.....	2.0
		Turkey-fat.....	5.6

POLENSKE VALUE OF BUTTER-FAT.

VALUES FOUND BY E. POLENSKE.			VALUES FOUND BY M. FRITZSCHE		
Reichert-Meissl Value.	Normal Pol. Value.	Maximum Limit.	ON DUTCH BUTTER.		
c.c. N/10 KOH.	c.c. N/10 KOH.	c.c. N/10 KOH.	Reichert-Meissl Value.	Normal Pol. Value.	Maximum Limit.
			c.c. N/10 KOH.	c.c. N/10 KOH.	c.c. N/10 KOH.
20-21	1.3-1.7	2.1	30-31	2.1-3.2	3.2
21-22	1.4-1.8	2.2	31-32	1.9-3.2	3.2
22-23	1.5-1.9	2.3	32-33	2.1-3.4	3.4
24-45	1.7-1.8	2.3	33-34	2.5-2.9	3.4
25-26	1.8-1.9	2.4			
26-27	1.9-2.0	2.5			
27-28	2.0-2.2	2.7			
28-29	2.2-2.5	3.0			
29-30	2.5-3.0	3.5			

KÖTTSTORFER SAPONIFICATION VALUE.

	Mg. KOH per Gram.		Mg. KOH per Gram.
Butter.....	216-233	Sperm.....	123-147
Oleomargarine.....	192-200	Rape.....	167-179
Cocoanut-oil.....	246-270	Cocoa-butter.....	192-202
Lard.....	193-200	Sesame.....	187-193
Olive-oil.....	187-195	Wool-fat.....	98-127
Niger-oil.....	189-191	Almond.....	187.9-195.5
Linseed-oil.....	190-195	Peanut.....	185.6-197
Cottonseed-oil.....	191-196	Palm.....	202
Castor.....	176-186	Beeswax.....	90-100
Cod-liver oil.....	171-189	Mustard-oil.....	170-180

HEHNER VALUE.

AVERAGE PERCENTAGE OF INSOLUBLE ACIDS.

Butter.....	87.5	Cod-liver oil.....	95.46-97.05
Cocoanut-oil.....	86.43	Almond-oil.....	96.6
Palm-nut oil.....	91.1-95.6	Cocoa-butter.....	94.59
Lard.....	96.15	Tallow.....	95.50
Oleomargarine.....	95.56	Cottonseed.....	95.75
Olive.....	95.43	Peanut-oil.....	95.00
Rape.....	95.10	Sesame.....	95.48

* De Negri and Fabris have found as low a number as 3.

MAUMENE NUMBER OF OILS.

		Authority.
Linseed.....	103	Maumene
“	104-124	Baynes
“	104-111	Allen
“	122-126	De Nigri and Fabris
Niger.....	82	Baynes
“	81	Allen
Cottonseed (raw).....	84	Baynes
“ “	61	Dobb
“ “	70	Archbutt
“ “	67-69	De Nigri and Fabris
Cottonseed (refined).....	77	Baynes
“ “	75-76	Archbutt
“ “	74-75	Allen
Sesame.....	68	Maumene
“	65	Archbutt
“	63-64	De Nigri and Fabris
Colza.....	57-58	Maumene
“	54-56	Dobb
“	55-64	Archbutt
“	51-60	Allen
“	49-51	De Nigri and Fabris
Almond.....	52-54	Maumene
“	51-53	De Nigri and Fabris
Peanut.....	67	Maumene
“	47-60	Archbutt
“	45.5-51	De Nigri and Fabris
Olive.....	42	Maumene
“	40	Baynes
“	39-43	Dobb
“	41-45	Archbutt
“	41-43	Allen
“	32-37	De Nigri and Fabris
Castor.....	47	Maumene
“	46	Archbutt
“	46-47	De Nigri and Fabris
Lard-oil.....	36	Olsen and Benoit

SPECIFIC TEMPERATURE NUMBER OF OILS.*

		Authority.
Linseed.	320-349	Thomson and Ballantyne
"	313	Jenkins
Cottonseed.....	163-170	Thomson and Ballantyne
"	174.3	Tolman and Munson
" butter-oil.	172.9	" " "
" summer white....	191.1	" " "
" cooking-oil.	192.4	" " "
" blown.	164	Jenkins
Colza.	125-144	Thomson and Ballantyne
"	130	Jenkins
Rape.	135.6-152.5	Tolman and Munson
Peanut.	105-137	Thomson and Ballantyne
"	129.1-135.3	Tolman and Munson
Olive.....	89-94	Thomson and Ballantyne
"	94	Jenkins
"	94.5-109.7	Tolman and Munson
Boiled linseed.	248	Jenkins
Castor.	89	Thomson and Ballantyne
Sperm.	100	" " "
Cocanut.	44	Tolman and Munson
Lard-oil.	96.0	Olsen and Benoit
Mustard (black).	189.4	Tolman and Munson
" (brown).	165.4	" " "
" (black).	169.3	" " "
" (yellow).	130.9	" " "
Almond.	117.6	" " "
Sunflower.	166.7	" " "
Maize.	190.2	" " "

ACETYL VALUE OF OILS.

Linseed.	8.5	Whale-oil (old).	23.1
Sesame.	11.5	" (recent).	13.2
Cottonseed.	16.6	" (various sam-	
Colza.	6.3	ples).	11.6-17.2
Almond.	5.8	Grape-seed.	144.5
Peanut.	3.4	Cod-liver oil.	41.1-50.6
Olive.	10.6	Seal-oil.	33.0-33.9
Castor.	153.4-156		

* This modification of Maumene's test being comparatively new, there are less data of results to choose from than is the case with the older methods.

CHAPTER XXXI.

GAS ANALYSIS.

695. General Methods of Gas Analysis.—Two general methods are in use for the analysis of gases. The gas to be determined may be absorbed in an appropriate liquid and the amount determined by **VOLUMETRIC** or **GRAVIMETRIC METHODS**. The determination of carbon dioxide illustrates these methods. This gas may be absorbed in caustic potash solution in a Liebig bulb which is weighed before and after absorption. It may also be absorbed in a measured volume of standard barium hydroxide solution and the excess of alkali titrated with standard acid. Such methods should always be used when the gas to be determined is mixed with a large amount of other gases, as is the case with carbon dioxide in the air.

If the gas to be determined constitutes a relatively large proportion of a gaseous mixture, its amount may be ascertained by taking a **MEASURED VOLUME** of the gaseous mixture and measuring the residue after the constituent to be determined has been absorbed. Such determinations may be made very rapidly and with a high degree of accuracy, the methods having been well developed and excellent apparatus devised by Bunsen, Hempel, and others.

ABSORBENTS FOR OXYGEN.

Two reagents are commonly in use for absorbing oxygen in gas analysis—an **ALKALINE SOLUTION OF PYROGALLOL** and **YELLOW PHOSPHORUS IN STICKS**.

696. The Pyrogallol, being in solution, may be used in apparatus of a great variety of form. The solution must not be used at a temperature less than 15° , since at lower temperatures the

absorption of oxygen is very slow. The absorption is not complete unless a large excess of the reagent is present. When the solution has absorbed a few per cent of the amount of oxygen which it will take up, it leaves, during subsequent use, a larger and larger residue of unabsorbed oxygen in the gas which is in contact with it. A solution which has been exposed to the air for even a short time must therefore not be used. A record should be kept of the amount of oxygen absorbed by a given solution, so that it may be discarded when no longer efficient. The solution is made according to Hempel * by dissolving 5 grams of pyrogallol in 15 c.c. of water and adding 120 grams of caustic potash dissolved in 80 c.c. of water. The caustic potash purified by alcohol should not be used. 1 c.c. of this solution will absorb completely 2 c.c. of oxygen.

697. Yellow Phosphorus has the advantage that its absorbing power is practically unlimited. It should be protected from the light, which converts it into the red inactive modification. It is fully as efficient an absorbent of oxygen as the solution of pyrogallol. It is kept in a gas pipette under water, which, besides protecting it from the oxygen of the air, serves to dissolve the oxides of phosphorus produced during the absorption of the oxygen. As these oxides are solid and have practically no vapor tension it is not necessary to wait for their absorption before reading the volume of the residual gas. The temperature of the phosphorus must not be allowed to fall below 15° or the absorption will be very slow, 20° being a more favorable temperature.

698. Pure Oxygen at atmospheric pressure is not absorbed by phosphorus. If the oxygen is diluted by admixture with another gas or the pressure reduced by means of an air-pump, action begins when the pressure of the oxygen is 75% of atmospheric pressure. The action is then violent, being accompanied by the evolution of light and heat, so that the phosphorus is melted. A gas containing more than 50% of oxygen should not be brought into contact with the phosphorus. If a gas containing more than this amount of oxygen is to be analyzed, it may be diluted with nitrogen which is prepared from air by absorption of the oxygen

* Gas Analysis, 1902, p. 149.

by phosphorus. The absorption of oxygen is entirely or partly prevented, according to Schönbein, by the presence of ethylene and other hydrocarbons, ethereal oils, alcohol, and traces of ammonia.

699. The Phosphorus is Formed into Sticks by melting a sufficient amount in a test-tube under a layer of water. The test-tube is most conveniently heated by placing it in warm water. Glass tubes having an internal diameter of 2 to 3 mm. are selected and inserted into the test-tube with the larger end down. It will be found that the diameter of most glass tubing varies so that tubes having a slight difference in diameter at the two ends may easily be found. On placing the finger over the upper end of the glass tube and taking it out it will remain filled with phosphorus, which may be solidified by holding the tube in cold water. If, on cooling, the stick of phosphorus does not drop out on tapping the tube, it may be shoved out with a stiff wire. The operation is more easily performed if a short piece of rubber tubing with a pinch-cock is placed on the upper end of each glass tube. While one tube is cooling in the water others may be filled with phosphorus.

700. Chromous Chloride.—Oxygen may also be quantitatively absorbed by a solution of chromous chloride, which does not absorb hydrogen sulphide nor carbon dioxide.

701. For the Absorption of Carbon Dioxide a solution of caustic potash is used. It is made by dissolving 1 part of commercial caustic potash in 2 parts of water. 1 c.c. of this solution will absorb quantitatively 40 c.c. of carbon dioxide.

ABSORBENTS FOR CARBON MONOXIDE.

This gas is absorbed by CUPROUS CHLORIDE dissolved in HYDROCHLORIC ACID or in AMMONIA. As solutions of cuprous chloride rapidly absorb oxygen from the air, the cuprous chloride being converted into cupric chloride, the solution must be protected from the atmosphere. Hydrochloric acid solutions may be kept reduced by the presence of metallic copper, the most convenient form being wire gauze. Any cupric chloride formed in such a solution is slowly reduced to cuprous chloride by the metallic

copper, which dissolves, the brown solution becoming colorless. If the hydrogen in a mixture of gases is to be absorbed by palladium after the absorption of the carbon monoxide, the ammoniacal solution must be used.

702. The Absorbing Power of neither solution is large, and the carbon monoxide is held in such loose combination that after a moderate amount has been absorbed the solution gives up a small part of the carbon monoxide again to a gas in which it is absent. As acetylene and ethylene are also absorbed by cuprous chloride solutions, these gases must be removed before determining carbon monoxide. This is accomplished by the absorbents used to determine the "heavy hydrocarbons" or "illuminants."

703. The Hydrochloric Acid Solution of Cuprous Chloride may be made, according to Winkler,* by adding a mixture of 86 grams of copper oxide and 17 grams of finely divided metallic copper to 1086 grams of hydrochloric acid (sp. gr. 1.124), the mixture being slowly introduced and the acid frequently stirred. The copper powder is best prepared by reducing copper oxide in a stream of hydrogen. The solution should be placed in a flask which it very nearly fills. A spiral of copper wire is introduced into the flask, which is closed with a rubber stopper and allowed to stand in the dark until the color has disappeared. 1 c.c. of this solution will absorb 4 c.c. of carbon monoxide.

The solution may also be made by dissolving 15 grams of commercial cuprous chloride in 120 c.c. of concentrated hydrochloric acid. Twenty grams of copper drillings are added, and the solution is allowed to stand twenty-four hours. It is diluted with water to 200 c.c. and decanted from the metallic copper for use.

704. The Ammoniacal Solution of Cuprous Chloride may be prepared by placing 15 grams of commercial cuprous chloride in a 250-c.c. flask and adding 200 c.c. of 7% ammonia. After inserting the stopper the solution is shaken until the cuprous chloride is dissolved.

705. The Cuprous Chloride may be prepared by dissolving 30 grams of copper sulphate and 15 grams of sodium chloride in 100 c.c. of water. Sulphur dioxide is passed into this solution

* Hempel, Gas Analysis, 1902, p. 202.

until precipitation is complete. The solution is decanted and the cuprous chloride is washed several times by decantation and dissolved in ammonia or hydrochloric acid as desired.

ABSORBENTS FOR THE "ILLUMINANTS."

Ethylene and its homologues, as well as benzene and its homologues, which taken together are known as *heavy hydrocarbons* or *illuminants* in the analysis of illuminating-gas, are absorbed by FUMING SULPHURIC ACID OR BROMINE-WATER.

706. The Fuming Sulphuric Acid gives off vapors of sulphur dioxide and trioxide, so that after absorption of the hydrocarbons the gas remaining must be passed over caustic potash to free it from the acid vapors. The fuming sulphuric acid must contain a large amount of sulphur trioxide and should on cooling deposit crystals. The commercial acid is seldom strong enough. It may be concentrated by distilling the sulphur trioxide from one portion into a second portion. The distillation should be conducted in a tubulated retort, using as a receiver a flask the neck of which fits quite snugly over the stem of the retort. The flask may be placed in a large funnel to the stem of which is attached a rubber tube leading to the sink. A stream of water is allowed to flow over the flask. If crystals form in the receiver, they may be dissolved at the end of the distillation by gently warming the flask. The distillate should be exposed to the air as little as possible. One c.c. will absorb 8 c.c. of the illuminants.

707. If Bromine is used as the absorbent, a few cubic centimeters of liquid bromine are placed in the absorption pipette and distilled water added. On shaking, the water becomes saturated with bromine. When the gas containing heavy hydrocarbons is introduced the bromine fumes above the water disappear. On shaking the liquid more bromine vapors appear, only to be again absorbed until all the heavy hydrocarbon vapors have been removed, when the bromine fumes persist and may be removed by passing the gas over caustic potash. According to Cl. Winkler,*

* Zeit. f. anal. Chem., 28, 269.

the absorption of ethylene by means of bromine is not as complete as by fuming sulphuric acid.

708. Absolute Alcohol.—According to Hempel and Dennis,* benzene and its homologues may be absorbed by absolute alcohol, 1 c.c. being sufficient for 100 c.c. of illuminating-gas. The alcohol is placed in a pipette over mercury. The alcohol vapor is afterwards removed by washing the gas with 1 c.c. of water. As these vapors are soluble in caustic potash, they should be absorbed before passing the gas over caustic potash, otherwise the result for carbon dioxide will be high and for heavy hydrocarbons low.

DETERMINATION OF HYDROGEN.

No liquid absorbent for hydrogen is known. It is determined by adding a sufficient amount of oxygen to form water with the hydrogen present and igniting the mixture. The volume of the mixed gases being measured before and after combustion, the diminution in volume is noted. If the gas was saturated with water vapor before combustion, two-thirds of this diminution will represent the volume of hydrogen present, since two volumes of hydrogen unite with one volume of oxygen, and the water formed occupies no volume except that necessary to saturate the gases present with water vapor.

709. Explosion of Hydrogen and Oxygen.—Various methods are in use for causing the union of the hydrogen with the oxygen. The method longest in use consists in producing an explosion in the gas mixture by means of an electric spark. The electric current is led in through platinum wires fused into the glass of which the confining vessel is made.

The proportion of *explosive gases* present to *non-explosive* must for various reasons be carefully regulated. By explosive gases is meant the combined volume of oxygen and hydrogen in the proportion to form water. Any hydrogen or oxygen present in excess constitutes a non-explosive gas, as well as nitrogen, carbon dioxide, etc. If all or nearly all of the gas present were explosive,

* Journ. für Gasbel., 1891, p. 414.

the action would be so violent as to shatter the confining vessel. If not violent enough to shatter the vessel, another difficulty would be encountered in that if any nitrogen were present some of it would be oxidized, giving a greater diminution in volume than corresponds to the amount of hydrogen present. On the other hand if the explosion were too weak, the combustion of the hydrogen would be incomplete. According to Bunsen there should be present for 100 volumes of non-explosive gases at atmospheric pressure not less than 26, nor more than 60 volumes of explosive gases, while the most favorable proportion is 26 to 40 parts of explosive gas to 100 parts of non-explosive.

If an insufficient amount of the explosive gas is present, oxygen gas produced by the electrolysis of water may be added. As this gas is entirely converted into water on explosion, the exact amount added need not be noted. If the proportion of explosive gas is too great, air or pure oxygen may be added. Whenever a gas poor in hydrogen is to be analyzed, the required amount of oxygen should be added in the form of the pure gas. This may be produced according to Bunsen by blowing a small retort from glass tubing and half filling it with pure powdered potassium chlorate. The oxygen is evolved by heating the bulb with the Bunsen burner, the first portions being discarded because contaminated with air. If the gas to be analyzed contains a large percentage of hydrogen, air should be used to furnish the oxygen.

710. Slow Combustion of Hydrogen.—Because of the large amount of inert gas which must be present to diminish the violence of the explosion, only small amounts of the gas to be analyzed can be operated upon when it is exploded. This difficulty is obviated by the method proposed by Dennis and Hopkins,* by which the combustion is effected by means of a red-hot platinum wire. Pure hydrogen may be burned by this method. It is introduced into the pipette containing the red-hot platinum wire, and a mixture of equal parts of air and oxygen containing more oxygen than sufficient to combine with the hydrogen is introduced slowly into the pipette containing the hydrogen. The

* Jour. Am. Chem. Soc., 21, 398.

hydrogen is burned almost as rapidly as the necessary oxygen is introduced.

711. Combustion of Hydrogen by Palladium Sponge.—The mixture of hydrogen and oxygen may also be burned by passing the gas over palladium sponge or palladium asbestos,* which is prepared as follows: One gram of palladium is converted into chloride, and the solution treated with a few cubic centimeters of a saturated solution of sodium formate, and enough caustic soda to make the solution strongly alkaline. One gram of fine silky asbestos is immersed in the solution, which should be entirely taken up by the asbestos. The material is dried by gently heating on the water-bath. The palladium is deposited on the asbestos, to which it adheres firmly. The asbestos is placed in a funnel and thoroughly washed with hot water and again dried. This asbestos may be twisted into threads by moistening with water and inserted into capillary tubes and again dried on the water-bath before being used.

712. Theory of Combustion of Hydrogen by Palladium Sponge.—The palladium is able to absorb large quantities of hydrogen, especially at high temperatures. When air is led over palladium saturated with hydrogen, water is formed, and the combustion is so energetic that the palladium becomes red-hot, and in this condition it is superficially oxidized. If hydrogen is led over this palladium, even at the ordinary temperature, it is burned at the expense of the oxygen of the palladous oxide. If the hydrogen has previously been mixed with pure oxygen or air, the palladium which has been heated by the combustion of some of the hydrogen with the oxygen of the palladous oxide is able to absorb more hydrogen, which then can combine with the gaseous oxygen present. When all of the hydrogen present has been burned a film of palladous oxide will be formed on the hot palladium by the excess of oxygen present, when the palladium will be in condition for the next combustion, and the oxidation will begin at the ordinary temperature. If the palladium has not been rendered active in this manner, it must be heated to 100° , or even to redness, before action begins, the hydrogen being absorbed more readily

* Cl. Winkler, *Technische Gas-Analyse*, p. 86.

at high temperatures, and the film of oxide being always formed when the palladium is heated to redness in the presence of oxygen.

713. Temperature.—As methane is also oxidized when a mixture of oxygen and hydrogen containing this gas is passed over palladium heated to 200° or higher, it is advisable to heat the palladium only to 100° when methane is present, in order to effect the combustion of the hydrogen alone. The tube containing the palladium is placed in boiling water and the mixture of gases is led through it very slowly, so that the temperature shall not rise to 200° .

714. Determination of Methane by Combustion.—As no absorbent for methane is known, this gas must also be determined by combustion with oxygen. The explosion by means of the electric spark and the combustion with the red-hot platinum wire may be used exactly as given for hydrogen. The same precautions must be taken in regard to the proportion of explosive to non-explosive gas. It must be remembered that one volume of methane requires for its combustion two volumes of oxygen. The volume of methane will be equal to one-half of the contraction noted after the explosion, provided all other combustible gases are absent. The volume of methane will also be equal to the volume of carbon dioxide present after the explosion, provided all carbon dioxide and all gases which produce carbon dioxide on combustion are removed before the explosion.

715. A Mixture of Hydrogen and Methane may readily be analyzed by combustion. The contraction produced is noted, and then the amount of carbon dioxide present is determined. The volume of methane will be exactly equal to the volume of carbon dioxide produced, as 1 molecule of each of these gases contains 1 atom of carbon. Twice the volume of methane, or of the carbon dioxide found, is the contraction due to the combustion of the methane. On subtracting this volume from the total contraction, that due to the hydrogen present is obtained, and two-thirds of this volume will give the amount of hydrogen present. By subtracting the combined volumes of methane and hydrogen from the original volume of the gas analyzed, the amount of NITROGEN or other gas present may be ascertained.

716. Determination of Nitrogen.—As no convenient method of absorbing nitrogen is known, this gas is generally determined by difference, all other gases having been absorbed or determined.

APPARATUS FOR THE ANALYSIS.

The apparatus used in gas analysis, of which a great variety has been devised, must provide for two essentially different operations, namely, the measuring of the gas and the absorption of individual constituents. The measuring of the gas volumes must be accompanied by observations of the temperature and pressure to which the gas is subjected.

717. Regulation of Temperature.—Almost invariably the gas is allowed to assume the temperature of the atmosphere of the work-room and the temperature is noted from a thermometer which is suspended near the measuring-tube. All sources of artificial heat are removed from the immediate proximity of the gas or from the room entirely. The heat emanating from the body and especially the hands of the operator is sufficient to appreciably change the volume of the gas unless precautions are taken to prevent it. For this reason the glass measuring-tubes are frequently water-jacketed, the temperature of water changing much more slowly than that of gases.

718. Regulation of Pressure.—The temperature of the gas being fixed as that of the atmosphere, the volume varies inversely with the pressure. In some forms of apparatus the pressure is kept constant, that of the atmosphere being generally used, the volume only being read, while in other forms both volume and pressure are carefully noted, the latter as well as the former being allowed to vary. Both the temperature and pressure of the atmosphere being quite constant for short intervals of time, gas analyses are frequently carried out in which the volume only of the gas is noted, the results being given in percentage by volume. In carrying out an analysis in which the weight of a gaseous constituent must be obtained, both temperature and pressure must be noted as well as the volume.

719. Confining Liquids.—Both WATER and MERCURY are used as the confining liquids in gas apparatus. The tension of mercury vapor at ordinary temperatures being very small and all gases being almost absolutely insoluble in this metal, it is almost an ideal confining liquid, and for some operations is indispensable. Because

of the slight solubility of most gases in water, the results obtained when this liquid is used are slightly inaccurate. The errors are considerably reduced, however, by using water which has been saturated with the gas to be analyzed. This is accomplished by shaking the water with a portion of the gas or by passing a stream of it through the water.

HEMPEL'S GAS APPARATUS.

Very convenient forms of apparatus have been perfected by Hempel. Water is used as the confining liquid and the measurements of volume are taken at atmospheric temperature and pressure.

720. The Simple Gas Burette consists of two glass tubes set in iron or loaded wooden feet, as shown in Fig. 66. The tubes are bent at right angles at the bottom and drawn out so as to afford convenient attachments for the rubber tube about 120 cm. long which joins them. The *measuring-tube A* ends in a capillary tube, *c*, over which a short piece of rubber tubing may be slipped. A Mohr pinch-cock, *d*, placed on this tube, makes a convenient and perfectly tight stop-cock. The tube is graduated in cubic centimeters, and is capable of holding 100 c.c. of gas, the lower mark being made a little above the foot. The numbers run both up and down. The second tube *B* is called the *level tube*, and serves to hold the confining liquid.

721. The Modified Winkler Gas Burette is similar in construction, except that a glass stop-cock is placed at both ends of the measuring-tube. The upper stop-cock *a* is the ordinary two-way stop-cock, while the one at the bottom, *b*, is a three-way cock, the third opening being through the key and the tube *c*. A rubber tube may be attached to this tube and gas admitted to the measuring-tube without coming in contact with the water in the level tube. This burette is used when the gas to be analyzed contains a constituent easily soluble in water. The tube is dried out by rinsing it with a little absolute alcohol and ether, the vapor of which is displaced by a stream of air. The three-way stop-cock is turned so that its horizontal opening communicates with the

inside of the burette, and by means of a tube attached to this opening the gas to be analyzed is passed through the burette until the air is entirely expelled. The three-way stop-cock is closed and then the upper stop-cock. The reagent for absorbing the soluble gas is then introduced into the burette through a

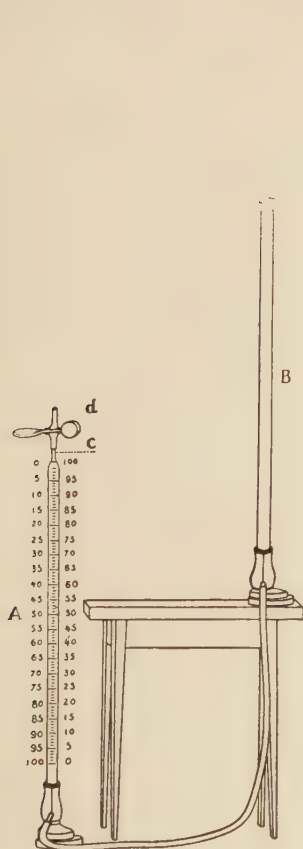


FIG. 66.

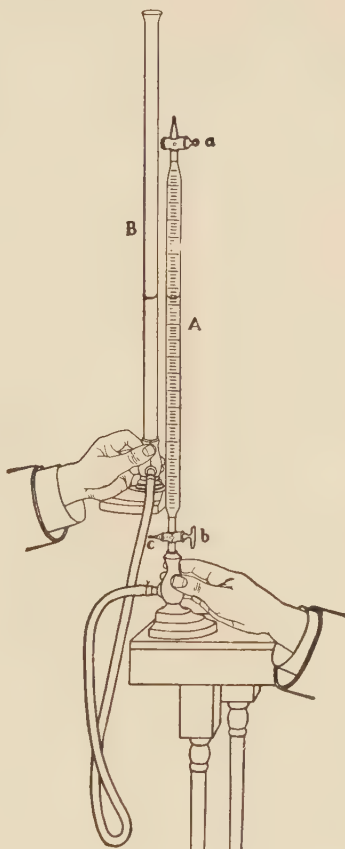


FIG. 67.

funnel attached to the horizontal opening *c* in the three-way stop-cock. After the absorption of this constituent the remainder of the analysis is conducted in the usual manner. Whenever possible the burette with the Mohr pinch-cock should be used in place of the Winkler burette, as glass stop-cocks are not as reliable as rubber tubing and a pinch-cock.

722. The **Absorption Pipette** in its simplest form is shown in Fig. 68. It consists of two bulbs, *a* and *b*, having capacities of 100 c.c. and 150 c.c. respectively. A capillary tube, *c*, bent into a U-shape is sealed to the bulb *b*, and the whole is fastened to the iron stand. This pipette is used for liquids which attack rubber and which do not need protection from the air, such as caustic potash and bromine-water. The bulb *b* is filled completely, while *a* is left empty, so that when the gas is introduced through the tube *c* into the bulb *b* the reagent expelled may pass into the bulb *a*.

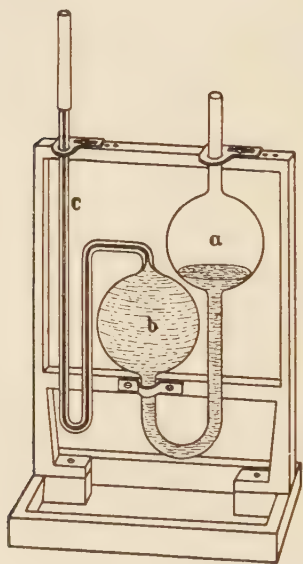


FIG. 68.

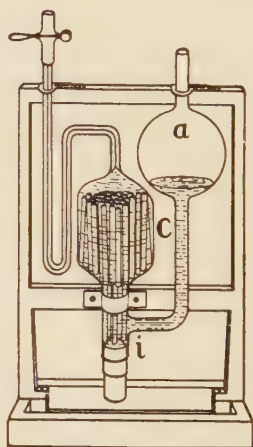


FIG. 69.

A modified form of this pipette which is suitable for solid reagents is shown in Fig. 69. After the solid has been introduced through *i* the opening is closed with a solid-rubber stopper, or, still better, with a closed glass tube of suitable size, over which a short piece of rubber tubing has been slipped. Very little rubber is then exposed to the action of the reagent. Whichever stopper is used, it should be firmly wired on. This pipette is suitable for the sticks of phosphorus used for the absorption of oxygen.

723. **The Double Pipette** is used for reagents, such as cuprous chloride, which must be protected from the air. The absorbing reagent is placed in the bulb *a*, and when this bulb is filled with gas the liquid is forced into the bulb *b*. The bulb *c* is filled with water, which serves to retain the atmosphere of nitrogen, carbon dioxide, or other indifferent gas which is kept in the bulb *b* over

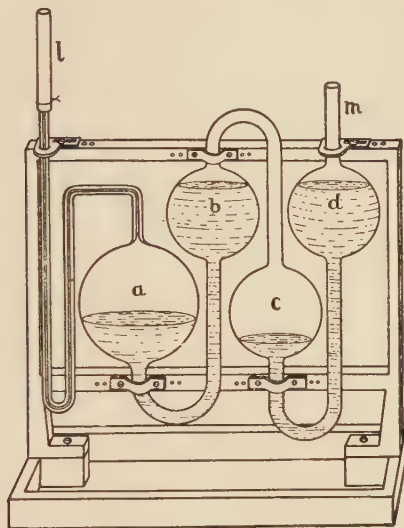


FIG. 70.

the reagent. To fill this pipette a stream of carbon dioxide or nitrogen is passed into the empty pipette at *m*. The stream of nitrogen may be produced by placing in a small flask a mixture of equal parts of ammonium chloride and sodium nitrite. After the flask has been attached to the pipette by means of a rubber stopper and a delivery-tube the nitrogen is evolved by gently heating the flask with the Bunsen burner. When the air has been displaced the delivery-tube is disconnected and the bulb *c* filled with water. A glass tube, about a meter long, is connected at *l* by means of a short piece of rubber tubing, and the cuprous-chloride solution transferred to the bulb *a* by pouring it into a funnel attached to the upper end of the long glass tube.

If FUMING SULPHURIC ACID is placed in a double pipette, the liquid seal in *c* and *d* should be concentrated sulphuric acid. Any water in the bulbs may be rinsed out with concentrated sulphuric

acid. On account of the action of the fuming sulphuric acid on rubber the pipette must be filled by inverting it so that the end of the capillary tube may be dipped into the acid. Suction is applied by the lungs or a Bunsen filter-pump at *m* until the bulb *a* is full. The pipette is then inverted and concentrated sulphuric acid poured into the bulb *d* to prevent the entrance of moisture from the atmosphere.

724. The Double Pipette for Solid and Liquid Reagents has an opening in the bulb *a* for the insertion of solids. This bulb is used for the acid cuprous chloride solution. The bulb *a* is filled with glass tubes containing coils of copper wire. After pouring in the cuprous chloride solution the opening is closed with a rubber stopper or glass stopper as directed for the single pipette for solid reagents. This bulb need not be filled with nitrogen, as any cupric chloride formed by the oxygen present is soon reduced by the metallic copper, the air in it being soon deprived of its oxygen.

725. The Explosion Pipette consists of a thick-walled glass bulb closed with a glass stop-cock at *d*. The level bulb *b* is connected

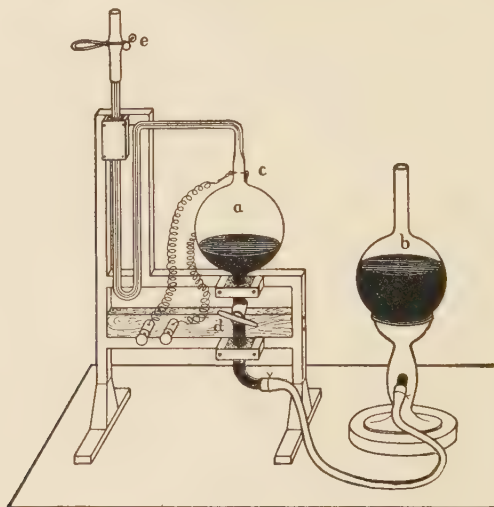


FIG. 71.

with the bulb *a* by means of a piece of thick-walled rubber tubing. Mercury is used as the confining liquid in the pipette, since under the high pressure developed by the explosion a considerable amount

of carbon dioxide would dissolve in water. Platinum wires are sealed into the glass at *c*. The spark which ignites the gases is produced between these wires. The current from several Bunsen dichromate cells or other convenient battery is passed through a Ruhmkorff induction-coil. A coil about 15 cm. long is of convenient size. The secondary current produced by the induction-coil should produce a bright spark between the platinum wires. A box made of strong wire netting is very convenient for placing over the pipette for protection in case it should be shattered by the explosion. If this is not at hand, it should be placed in a hood or covered with a towel during the explosion.

726. The Pipette Arranged for Combustion with a Hot Platinum Wire is shown in Fig. 72. A stout iron wire inclosed in a glass

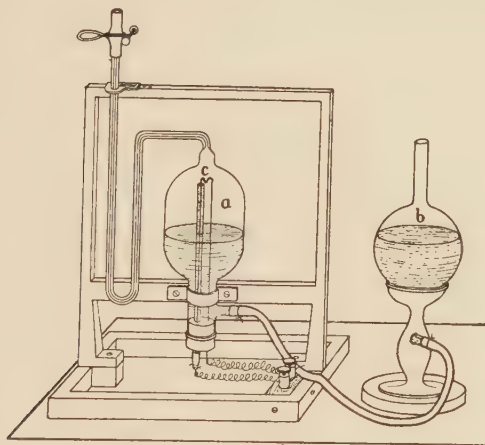


FIG. 72.

tube is pushed through the rubber stopper and the lower end of the glass tube closed with a piece of rubber tubing which is wired around the iron wire. A second stout iron wire is pushed through the rubber stopper and the upper end connected with the first iron wire by means of a coil of platinum wire $\frac{1}{4}$ mm. in diameter. The coil should be about 2 mm. in diameter and contain from 20 to 30 turns. After filling the bulb with mercury or water the air is sucked out of the glass tube containing the iron wire by closing the capillary tube with a rubber tube and pinch-cock and applying suction with a pump to the tube of the level bulb. The gas to be

burned is transferred to the pipette, and a measured volume of oxygen is slowly passed into the pipette after heating the platinum wire to redness with a current of electricity.

727. The Method of Manipulation of the Hempel apparatus will be more fully understood from the following description of the analysis of illuminating-gas.

EXERCISE 74.

Analysis of Illuminating-gas.

728. Collecting the Sample.—200 c.c. of water are placed in a convenient-sized flask, and the gas to be analyzed allowed to bubble through for a few minutes, the flask being occasionally shaken. The level tube of the gas burette is filled with the water saturated with the gas, and the air displaced from the measuring-tube by opening the pinch-cock and raising the level tube. The measuring-tube is connected with the gas-supply by means of a rubber tube, from which the air is expelled by allowing the gas to flow a few minutes. If the gas has not been burned for some time, it should be allowed to flow for a few minutes in order to sweep out any air which has accumulated in the supply-pipes, which are seldom gas-tight. More than 100 c.c. are drawn into the measuring-tube by lowering the level tube. The pinch-cock of the measuring-tube is closed, and the tube connecting with the gas-supply is removed. Exactly 100 c.c. of the gas is obtained by holding the level tube in the hand, so that the bottom of the meniscus of the water is exactly opposite the 100-c.c. mark on the burette. The pinch-cock is now opened for a moment, thus allowing the excess of gas to escape. If the gas does not measure exactly 100 c.c. when the level tube is held so that the water is on the same level in the two tubes, the operation is repeated. After a little practice the exact amount of gas is readily obtained. The gas measuring-tube should be handled as little as possible. By taking hold of the foot heating the glass, and consequently the inclosed gas, is avoided.

729. Carbon Dioxide.—The burette is now connected to the caustic potash bulb, as shown in Fig. 73. The capillary tube *F* is inserted into the rubber tube *d* to the pinch-cock. The rubber tube *m* is then pinched with the fingers to expel the air, and the other limb of the capillary tube inserted. After noting the height of the caustic potash solution in the long arm of the capillary U-tube of the pipette, the gas is passed into the pipette by opening the pinch-cock and raising the level tube *B*. The pinch-cock is closed, and three minutes allowed for the absorption of the carbon dioxide, the pipette being shaken occasionally. The gas is then passed back into the burette by opening the pinch-cock and lowering the level tube, the caustic potash solution being brought to the same point in the capillary tube to which it came before passing in the gas. The pinch-cock is closed, and after three

minutes the volume of the gas is read by bringing the water in the two tubes to the same level by raising or lowering the level tube. The three-minute intervals are most readily gauged by means of a small three-minute sand-glass.

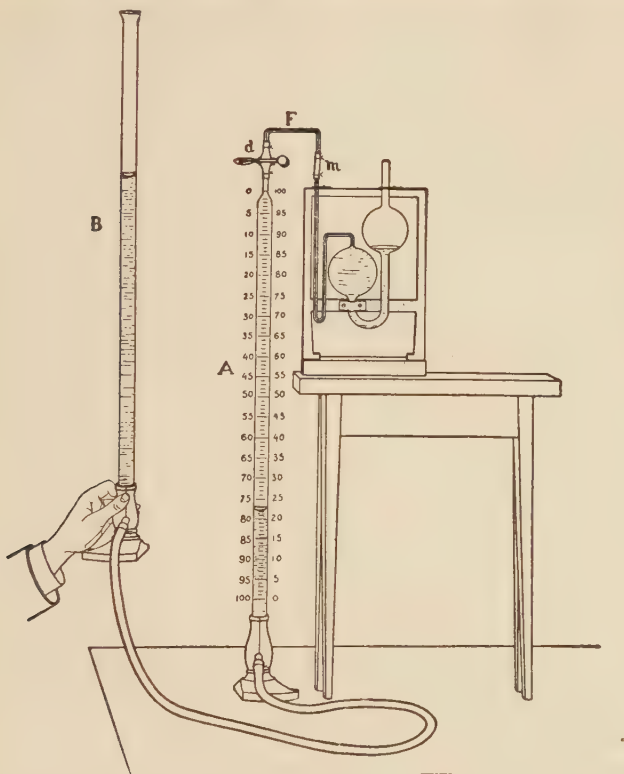


FIG. 73.

730. Illuminants.—While waiting three minutes for the water to run down in the burette and the gas to reach the atmospheric temperature, the caustic potash pipette should be replaced by the pipette containing the fuming sulphuric acid. After reading and recording the volume, the gas is passed over the fuming sulphuric acid and shaken for three minutes. The gas is then passed back into the measuring-burette, and once more passed into the caustic potash bulb, then back into the burette and measured after three minutes. If the white fumes of the oxides of phosphorus do not appear oxygen is absent or the phosphorus is too cold.

731. The Oxygen is absorbed by passing the gas into the phosphorus pipette. After three minutes it is passed back into the burette and measured.

732. The Carbon Monoxide is absorbed by passing the gas into the pipette containing the cuprous chloride solution. If this solution is fresh, the carbon

monoxide will be completely absorbed after shaking for three minutes, and the residue may be passed into the burette and measured. If a fresh solution of cuprous chloride, and also one which has been used considerably, are at hand, the bulk of the carbon monoxide may be absorbed by shaking for two minutes with the old solution, and the last traces absorbed by shaking the gas with the fresh solution for three minutes. A careful record should be kept on a piece of paper pasted on these pipettes of the amount of carbon monoxide absorbed. If a hydrochloric acid solution of cuprous chloride is used, the gas should be passed into the caustic potash bulb before measuring in order to remove the hydrochloric acid gas.

733. Explosion of Hydrogen and Methane.—The gas now remaining consists of methane, hydrogen, and nitrogen. These constituents may be determined by explosion, or by combustion with the red-hot platinum wire. If the explosion pipette is to be used, the gas is passed back into the cuprous chloride pipette, which is closed with a rubber tube and a pinch-cock. The water in the burette is replaced by distilled water which has been saturated with air. From 12 to 15 c.c. of the gas residue is then drawn into the burette and carefully measured. Air is then drawn into the burette until the total volume of the gas is very nearly 100 c.c. The volume is again carefully read and the gas is passed into the explosion pipette, the large bulb of which, including the capillary tube, has been filled with mercury. When the gas has been passed in, enough water to nearly fill the capillary tube should also be forced over and the glass stop-cock of the pipette closed. A pinch-cock is placed on the rubber tube, which is securely wired on the capillary tube of the pipette. The end of this rubber tube is also closed with a piece of glass rod. After placing the pipette under the hood or other safe place, the secondary coil of the Ruhmkorf coil is connected with the platinum wires of the explosion pipette, and the primary coil is connected with several Bunsen or other cells connected in series. The explosion should be vigorous enough to present a single flash of light, the course of which cannot be followed by the eye across the bulb. The glass stop-cock of the pipette is opened, and the gas passed into the burette, and after three minutes the volume is read. The burette is then connected with the caustic potash pipette, the carbon dioxide absorbed, and the volume of the gas again determined with the burette.

If the explosion was not satisfactory the operation should be repeated, using a little more of the gas residue. As this operation is attended with considerable liability of error, it is well in any case to repeat the explosion.

734. Combustion of Hydrogen and Methane by Red-hot Platinum Wire.—If the pipette fitted with the platinum wire for burning the gas is at hand, it should be used rather than the explosion pipette. The entire gas residue may then be used. After being carefully measured, it is transferred to the pipette containing the platinum wire heated to redness. 10% more oxygen than the volume of the gas residue is carefully measured in the burette, and then slowly passed into the pipette, the wire having been heated to redness by a suitable current of electricity. The oxygen used must be freed from carbon dioxide by passing through strong caustic potash solution or

by being shaken in the caustic potash pipette. The presence of nitrogen is not objectionable. The amount of contraction as well as the volume of carbon dioxide formed must be noted as when the explosion pipette is used.

735. Calculation of the Analysis.—The following analysis indicates the method of recording and calculating the results:

Volume of gas taken.....	100.0 c.c.	
After absorption by caustic potash.....	97.4 c.c.	
Per cent of carbon dioxide.....		2 6
After absorption by fuming sulphuric acid.....	84.2 c.c.	
Per cent of illuminants.....		13.2
After absorption by phosphorus.....	83.9 c.c.	
Per cent of oxygen.....		.3
After absorption by cuprous chloride.....	56.6 c.c.	
Per cent of carbon monoxide.....		27.3
Taken for explosion.....	14 c.c.	
After addition of air.....	98.5 c.c.	
Volume after explosion.....	75.9 c.c.	
Contraction.....	22.6 c.c.	
Volume after absorption by caustic potash.....	69.9 c.c.	
Volume of carbon dioxide.....	6.0 c.c.	
Volume of methane in 14 c.c. residue.....	6.0 c.c.	
The methane in 56.6 c.c. is found by the propor-		
tion $14 : 56.6 : : 6 : x$,	$x = 24.3$ c.c.	
Per cent of methane.....		24.3
The contraction due to methane, being twice its		
volume, will be.....	12 c.c.	
Contraction due to hydrogen.....	$(22.6 - 12) = 10.6$ c.c.	
The volume of hydrogen, being two-thirds of this		
contraction, will be.....	7.1 c.c.	
The volume of hydrogen in 56.6 c.c. will be found		
by the proportion $14 : 56.6 : : 7.1 : x$, $x = 28.7$ c.c.		
Per cent of hydrogen.....		28.7
Per cent of nitrogen.....		3.6

The combined volume of methane and hydrogen being 53.0 c.c., the remainder, or 3.6 c.c., is considered to be nitrogen.

736. The Orsat Apparatus.—A very convenient and compact apparatus for gas analysis was devised by Orsat, and with a number of modifications is very largely in use in the form shown in Fig. 74. The measuring-burette *a* has a capacity of 100 c.c., although the graduations do not always extend over the enlarged portion at the top, the absorbable constituents in many cases amounting to less than 50% of the gas analyzed. This burette is

water-jacketed, so that the gas may quickly come to a constant temperature. The absorption-bulbs, *b*, *c*, and *d*, contain glass tubes so as to give a larger absorbing surface to the reagent. Each of these bulbs is connected with a bulb of the same capacity, which is only partially seen at the rear in Fig. 74. The reagent forced out of the bulb in front by the gas passes into the bulb in the rear. The bulb *b* is filled with caustic potash for absorbing

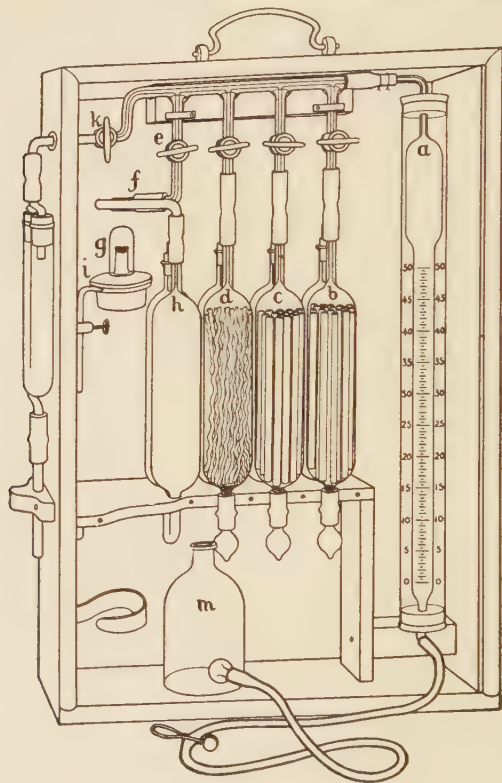


FIG. 74.

carbon dioxide, *c* is filled with an alkaline solution of pyrogallol for the absorption of oxygen, while *d* is filled with cuprous chloride solution for the absorption of carbon monoxide. The palladium tube *f*, with the alcohol-lamp *g* and the bulb *h*, to be used for the absorption of hydrogen, are not always attached, since the apparatus is very largely used for the analysis of flue gases in which hydrogen is absent. The large U-tube at the side is filled with

cotton, which removes dust particles from the gas as it enters the apparatus.

The bottle *m*, connected by means of a rubber tube with the measuring-tube, serves as a level tube, by which the gas may be forced into or out of the measuring-tube and absorption-bulbs. Water is used as the confining liquid. The whole apparatus is enclosed in a wooden case, the front and back of which may be readily removed.

737. The Manipulation of this apparatus is very similar to that of the Hempel apparatus. The stop-cocks and rubber joints must first be tested for leaks by bringing the solution in the absorption-bulbs to the zero-marks on the capillary stems and closing the stop-cocks. If after a few minutes the liquid has fallen in any of the bulbs, the stop-cock or rubber connection leaks, and the key of the former must be removed, cleaned, and lubricated with vaseline and the rubber joints made tight by wiring the rubber on the glass tubes. The stop-cock *k* and the rubber connections with the measuring-tube are tested by bringing the water in the measuring-tube to the zero-mark on the upper capillary by holding the level bottle at the same height. On closing the stop-cock *k* and lowering the bottle, no air should enter the apparatus as indicated by the height of the water-column when the bottle is again raised.

All of the joints having been made tight and the solutions in the absorption-bulbs being at the marks on the capillary stems, the measuring-tube is filled with the gas to be analyzed. In order to displace the air from the connecting-tubes it is necessary to fill the measuring-tube several times and then expel the gas. When a fair sample is finally obtained the volume is made exactly 100 c.c. by holding the bottle so that the level of the water is the same as that in the measuring-tube. The stop-cock *k* is then opened and immediately closed. The gas is then forced into the absorption-bulbs in turn and drawn back into the measuring-tube in order to note the diminution of volume. The absorption of oxygen and carbon monoxide being somewhat slower than that of carbon dioxide, it is well to pass the gas back into the same bulb after measurement to ascertain by a second measurement if absorption is complete. As the reagents

are not well protected from the air, they must frequently be renewed or tested for their efficiency.

738. In the Analysis of Flue Gases for judging the efficiency of the firing, the most difficult part of the operation is taking the sample of the gas. When the fires are hand stoked the composition of the flue gas will vary with the time which has elapsed since fresh coal was put on the grate, as the following analyses* show:

	One Minute After Stoking.	Twelve Minutes Later.
Carbon dioxide.	13.5	4.0
“ monoxide.	0.0	0.0
Oxygen.	5.5	16.5
Nitrogen.	81.0	79.5

739. Taking an Average Sample.—A very common practice consists in collecting the sample in a large bottle or gasometer from which the water is allowed to flow slowly, so that six, twelve, or twenty-four hours are required to fill the gas receiver. This average sample is then analyzed. When this method is used every precaution must be taken to make the connections absolutely tight and to shellac all rubber connections. The method is subject to the errors due to the solubility of the gases in the water used.

The tube extending into the flue may be of iron if the temperature of the gases is low. Should the iron become heated to even very dull redness alternate oxidation and reduction may take place, which very materially changes the composition of the gases. A glass or porcelain tube must then be used. Several openings should be made in the tube so that the gas in the entire cross-section of the flue may be sampled. The entrance to the flue should be made as near the fire as practicable, as the diffusion of both air and the products of combustion through the usual leaks in the flues is considerable.

740. Interpretation of Results.—The method of taking an average sample of the flue gases as already given is much more suitable for mechanically stoked fires than those hand fed. For the latter it is advisable to take numerous samples at various

* Lunge, Chem.-tech. Untersuchungsmethoden, Vol. I, p. 183.

intervals of time after stoking. The ideal flue gas should contain only carbon dioxide and nitrogen. The percentage of the former will not be quite equal to that of the oxygen in the air, because some of the oxygen combines with the hydrogen of the coal. The remainder of the oxygen, however, will give an equal volume of carbon dioxide, since a molecule of the latter contains a molecule of oxygen. Generally, however, the flue gases from even well-managed fires contain several per cent of unused oxygen. If oxygen is entirely absent and carbon monoxide is present, the draught of air is insufficient. Carbon monoxide may also occur in the presence of oxygen if clinkers are allowed to remain on the grate.

Problem 16.—A coal contains 3% hydrogen, 82% carbon, and 15% ash. What would be the composition by volume of the flue-gas (*a*) if perfect combustion took place, all the oxygen of the air being used up and no combustible left in the ash? (*b*) If only half of the oxygen of the air were used?

Problem 17.—A flue-gas produced by the same coal contains 3.3% carbon dioxide and 16.7% oxygen. Calculate the excess of air passing through the grate.

CHAPTER XXXII.

STOICHIOMETRY.

741. Atomic-weight Tables.—In the calculation of the results of many chemical analyses the atomic weight of one or more of the elements is used. The percentage found will vary somewhat according to the atomic weights used. Several tables of atomic weights compiled by various authorities are in use. Besides differing in the values assigned to elements whose atomic weights are in dispute, the tables differ as to the element whose atomic weight is taken as the basis for computing the remaining values. Until recently hydrogen has been taken as the basis, the value 1.000 having been assigned to it. Tables computed on the basis of 16.000 as the value for oxygen are now more commonly used. On this basis hydrogen has the value 1.008. It is advisable to select a set of atomic weights and in all calculations to use these values. The values used in this book are those given in Table I, p. 509, which is the table published by the International Atomic Weights Committee in 1908. The figures given by this Committee are based on the value for oxygen of 16.000, the values based on hydrogen as unity being no longer given.

742. Limit of Accuracy in Atomic Weights.—It will be observed that the number of figures given after the decimal point varies from one to three. This is due to the fact that the values have been determined with a varying degree of accuracy. In each case the last figure given is somewhat doubtful. The atomic weight of silver, for instance, is certainly between the values 107.9 and 108.0, the value 107.93 being the average of several determinations, in which the variations were in the second place of decimals. To write the atomic weight of silver with three figures after the decimal point, as 107.930, would be introducing an absolutely mean-

ingless figure. As most quantitative work is far less accurate than atomic-weight determinations, even the last figure given may frequently be dropped. Generally the figure 107.9 for silver will be near enough to its true value, the figure dropped representing only $\frac{1}{38500}$ of its atomic weight, which is smaller than the ordinary analytical errors. If in the same calculation the value of another element enters whose atomic weight is known with still less certainty, even one more figure may be dropped. If the atomic weight of iron, for instance, which is uncertain within 1 part in 560, enters into the calculation, the atomic weight 108 may be used for silver, the error being 7 parts in 10,793, or about 1 part in 1540. Numbers obtained by multiplying or dividing such numbers need not be given to more than four significant figures.

743. "Factors."—If iron has been precipitated as ferric hydroxide and weighed as ferric oxide the amount of iron in the precipitate is found by calculation, using the atomic weights of iron and oxygen. From the formula of ferric oxide, Fe_2O_3 , we know that 2 atoms of iron, or 111.8 parts, are combined with 3 atoms of oxygen, or 48 parts. In 159.8 parts of the precipitate there are present 111.8 parts of iron. If the weight of the precipitate is represented by p , the amount of iron, x , is found by the following proportion:

$$\text{Fe}_2\text{O}_3 : 2\text{Fe} :: p : x$$

$$159.8 : 111.8 :: p : x$$

$$x = \frac{111.8}{159.8} p.$$

The fraction $\frac{111.8}{159.8}$, which is equal to .6996, represents the percentage of iron in ferric oxide and enters into every calculation of the amount of iron as found by weighing ferric oxide. For each precipitate one or more factors are calculated in this manner, thus obviating the use of the proportion and simplifying the calculation. The factors for the commonly used precipitates are given in Table II, p. 510.

744. Logarithms.—To obtain the weight of a given element in a precipitate the weight of the precipitate is multiplied by the proper factor. The labor of multiplication may be greatly

lessened by using logarithms. For this reason the logarithms of the factors are also given in Table II. In order to *multiply* two numbers together their logarithms are *added*. The sum is the logarithm of the product of the two numbers. Two numbers may be *divided* by *subtracting* the logarithm of the divisor from the logarithm of the dividend, the remainder being the logarithm of the quotient. The abbreviation log. is frequently used for logarithm. The logarithms of the numbers from 1 to 9999 may be obtained from Table III, page 514. The logarithm of a number is composed of two parts, a mantissa and a characteristic. The former is a positive decimal fraction and is the same for any number composed of the same figures in the same order irrespective of the position of the decimal point. The characteristic is a positive or negative integral number and indicates the position of the decimal point of the number. In the first column at the left of Table III are found the natural numbers beginning with 10. The mantissas of the logarithms of any of these numbers are found in the next column headed 0. In the following columns are found the mantissas of the numbers formed by adding to those in the first column the significant figure which is found at the head of one of the columns. For instance, the mantissa of 21 is found in the column headed 0 opposite 21 and is .3222. In the next column opposite 21 is found .3243, which is the mantissa of 211. Following this number is .3263, which is the mantissa of 212. If the mantissa of a number of four places is desired the columns of differences must be utilized. The mantissa of 211 being .3243 and that of 212 being .3263, the mantissa of a four-place number between 2110 and 2120 will have a value between .3243 and .3263. The difference between these values is .0020, while the difference between 2110 and 2120 is 10. For each unit added to 2110, .0002 must be added to the mantissa of 2110, or .3243. The mantissa of 2115 is .3253, 10 having been added. This number may be found in the column of differences headed 5 opposite the natural number 21. As ordinary quantitative results are not accurate beyond four significant figures, there is no necessity of obtaining the mantissa to the fifth significant place.

745. The Characteristic is the number placed before the mantissa to designate the position of the decimal point in the

natural numbers. The characteristic of the log. of a number with one significant figure to the left of the decimal point is 0, if there are two figures it is 1, with three figures it is 2, etc. The characteristic of the log. of a decimal is a negative number and is equal to the number of places by which its first significant figure is removed from the place of units. In order to make this characteristic positive it is sometimes added to 10, which is placed with a minus sign after the mantissa. The logarithms may then be added, the proper number of tens being subtracted from the result. According to this rule the complete logs. of the numbers containing the figures 2115 are given in the following table:

Numbers.	Logarithms.	
2115.	3.3253	
211.5.	2.3253	
21.15.	1.3253	
2.115.	0.3253	
.2115.	$\bar{1}.3253$	or 9.3253-10
.02115.	$\bar{2}.3253$	or 8.3253-10
.002115.	$\bar{3}.3253$	or 7.3253-10

As the position of the decimal point may generally be ascertained by inspection of the numbers to be multiplied or divided, the characteristic is frequently omitted from the logarithms.

Illustration.—If a precipitate of ferric oxide weighing .3252 gram is obtained from .8276 gram of material, the percentage of iron is calculated by logarithms as follows:

	log. of .3252.	$\bar{1}.5122$	or	9.5122-10
	log. of factor of Fe in Fe_2O_3	$\bar{1}.8449$	or	9.8449-10
by addition	log. of weight of iron	$\bar{1}.3571$	or	19.3571-20
	log. of .8276.	$\bar{1}.9178$	or	9.9178-10
by subtraction and addition of 2(log. of 100)	log. of percentage of iron . .	1.4393	or	1.4393
	percentage of iron.	27.50		

The number corresponding to a given logarithm is obtained from the table of antilogarithms in exactly the same manner as the logarithm of a number is obtained from the table of logarithms, the first column of figures and the figures at the head of the other

columns being the logarithms, while the numbers corresponding are found in the body of the table.

746. Factors from a Single Precipitate.—A given precipitate may be used for the calculation of a large number of different substances, as is shown by the following indicated calculations based on determinations in which the weighed substance is barium sulphate. The weight of barium sulphate is indicated by p .

Substance weighed BaSO_4 .

Desired, the amount of barium.

$$\begin{array}{rcl} & \text{BaSO}_4 : \text{Ba} :: p : x \\ \text{Mol. wts.} & 233 & 137 \\ & x = \frac{137}{233}p; & \text{factor} = \frac{137}{233}. \end{array}$$

Desired, the amount of barium oxide.

$$\begin{array}{rcl} & \text{BaSO}_4 : \text{BaO} :: p : x \\ \text{Mol. wts.} & 233 & 153 \\ & x = \frac{153}{233}p; & \text{factor} = \frac{153}{233}. \end{array}$$

Desired, the amount of sulphur trioxide.

$$\begin{array}{rcl} & \text{BaSO}_4 : \text{SO}_3 :: p : x \\ \text{Mol. wts.} & 233 & 80 \\ & x = \frac{80}{233}p; & \text{factor} = \frac{80}{233}. \end{array}$$

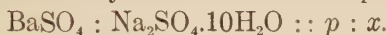
Desired, the amount of sulphuric acid.

$$\begin{array}{rcl} & \text{BaSO}_4 : \text{H}_2\text{SO}_4 :: p : x \\ \text{Mol. wts.} & 233 & 98 \\ & x = \frac{98}{233}p; & \text{factor} = \frac{98}{233}. \end{array}$$

Desired, the amount of sodium sulphate.

$$\begin{array}{rcl} & \text{BaSO}_4 : \text{Na}_2\text{SO}_4 :: p : x \\ \text{Mol. wts.} & 233 & 142 \\ & x = \frac{142}{233}p; & \text{factor} = \frac{142}{233}. \end{array}$$

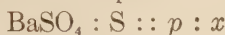
Desired, the amount of crystallized sodium sulphate.



Mol. wts. 233 322

$$x = \frac{322}{233}p; \quad \text{factor} = \frac{322}{233}.$$

Desired, the amount of sulphur.



Mol. wts. 233 32

$$x = \frac{32}{233}p; \quad \text{factor} = \frac{32}{233}.$$

747. The Calculation of the Theoretical Percentage of an Element in a Compound is made in exactly the same manner as the calculation of a "factor" where the element or radicle sought is part of the substance weighed. The theoretical percentage is the ratio of the atomic weight of the element sought to the molecular weight of the compound. For example, the theoretical percentage of silver in silver nitrate is obtained from the ratio $\frac{\text{Ag}}{\text{AgNO}_3}$, which equals $\frac{107.93}{169.94}$ or 63.51%.

The theoretical percentage of SO_4 in crystallized magnesium sulphate is obtained from the ratio $\frac{\text{SO}_4}{\text{MgSO}_4 \cdot 7\text{H}_2\text{O}}$, which equals $\frac{96.06}{246.532}$ or 38.96%.

748. Indirect Gravimetric Analyses are more difficult to calculate. General rules or factors cannot readily be given. The general method may be seen from the calculation of a determination of potassium and sodium in a mixture of the chlorides of these metals. This determination is readily carried out by weighing the sodium and potassium chlorides together and then determining the amount of chlorine present. As the percentage of chlorine in potassium chloride is 47.53, and in sodium chloride is 60.6, the percentage of chlorine in a mixture of these two salts will be between these numbers. For example, a sample of the mixed chlorides which weighed 1.5802 grams gave .9023 gram of chlorine, which is equal to 57.1 per cent. If only potassium chloride

had been present .7511 gram of chlorine would have been obtained. The difference between .9023 and .7511 is the amount of chlorine due to the presence of sodium chloride. This difference (.1512) divided by the difference in the percentage of chlorine in the two salts (.1307) gives the weight of sodium chloride present $\left(\frac{.1512}{.1307} = 1.1568\right)$. The weight of the mixed chlorides less the weight of sodium chloride gives the weight of potassium chloride present $(1.5802 - 1.1568 = .4234)$. The problem may be solved algebraically as follows:

Let x = the weight of sodium chloride;
 and y = " " " potassium chloride;
 then $x + y = 1.5802$ the weight of the mixed chlorides;
 and $.606x + .4753y = .9023$ the weight of chlorine.

Solving these simultaneous equations we find that

$$x = \frac{.9023 - (1.5802 \times .4753)}{.606 - .4753}.$$

On carrying out the indicated operations we obtain a value for x , or the amount of sodium chloride present, which is identical with that already obtained.

The disadvantage of using indirect methods of this kind is found in the fact that the difference upon which the weight of one of the constituents is calculated is very small. In the illustration given it must be multiplied by the factor $7.652 \left(\frac{1}{.1307}\right)$. The experimental errors of the analysis are increased in this ratio in the percentage found. The method is, therefore, not applicable to the determination of small amounts of one constituent in the presence of large amounts of the other.

749. Factor Weights.—When many determinations of a given constituent must be made it is found convenient to so choose the amount of substance to be weighed out that the weight of the precipitate obtained shall have a simple ratio to the percentage to be calculated. For example, if 1.373 grams of a substance containing .375 per cent of sulphur is weighed out, the sulphur converted into sulphuric acid and weighed as barium sulphate,

.0375 gram on the latter will be obtained. The number of milligrams of barium sulphate obtained is evidently equal to the hundredths of per cent of sulphur present. The general method of finding the amount to be weighed out in a given case may be obtained from the following general case:

Let w = the amount of substance weighed out;

and v = the weight of precipitate obtained;

and p = the per cent of the given constituent in the precipitate v .

The percentage is obtained by the following indicated calculations:

$$\frac{p \times v}{w}.$$

If the value of w bears a simple ratio to p , the percentage will bear a simple ratio to v . In the illustration already given p , or the percentage of sulphur in barium sulphate, is 13.73. w was made one-tenth of this number, or 1.373. The percentage is therefore ten times v or the weight of the barium sulphate obtained, as may be seen by substituting the values of v and w in the formula giving

$$\frac{v \times 13.73}{1.373}.$$

If w is made 13.73 grams, the weight of v in grams will be equal to the percentage of sulphur in the substance analyzed. In general, then, the amount of substance taken should bear a simple ratio to the percentage in the precipitate to be weighed of the constituent to be determined. This ratio will be inversely equal to the ratio of the percentage to the weight of the precipitate. For example, the percentage of chlorine in silver chloride being 24.72, the percentage of chlorine in a given substance will be ten times the weight of silver chloride obtained if 2.472 grams of the substance to be analyzed are weighed out.

CALCULATION OF THE FORMULÆ OF SALTS AND ISOMORPHOUS MIXTURES.

The results of many analyses may be expressed by a chemical formula. The composition of all pure chemical compounds as well as a large number of minerals may be expressed in this manner. All chemical formulas have been derived from quantitative anal-

yses and express primarily the proportions by weight in which the elements are present.

750. Salts.—Instead of using the percentage notation, the system of equivalent or atomic weights has been devised so that a single number or its simple multiple expresses the proportion in which a given element is present in its innumerable compounds. Sodium chloride, for example, contains 39.40 per cent of sodium, and 60.60 per cent of chlorine as found by analysis, but this fact is generally stated by giving the formula NaCl , which states that 23.05 parts of sodium are combined with 35.45 parts of chlorine. The ratio of the percentages 39.40 and 60.60 must be the same as the ratio of the numbers 23.05 and 35.45, and what is not quite so self-evident, the ratio of 23.05 to 39.40 must be the same as the ratio of 35.45 to 60.60. This ratio is 1.709; that is, 39.40 parts of sodium represent 1.709 atoms of this element and 60.60 parts of chlorine represent 1.709 atoms of chlorine. In this way it is found from the percentage composition and atomic weights that in sodium chloride an equal number of sodium and chlorine atoms are present. If the percentages of copper and chlorine found in crystallized cupric chloride are divided by the atomic weights of these elements the numbers

$$.5864 \quad \text{and} \quad 1.1728 \quad \left\{ \frac{37.30}{63.6} = .5864, \quad \frac{41.58}{35.45} = 1.1728 \right\}$$

are obtained. The number of chlorine atoms is evidently twice the number of copper atoms. The formula then must be CuCl_2 . The number of acid radicles, molecules of water, etc., may be found in the same manner, as may be seen from the calculation of the formula of potash alum from its analysis.

	Per Cent Found.	Atomic Weights	Atomic Ratios.
K.	8.17	39.14	$\frac{8.17}{39.14} = .2087$
Al.	5.78	27.1	$\frac{5.78}{27.1} = .2132$
SO_4	40.26	96.06	$\frac{40.26}{96.06} = .4190$
H_2O	45.74	18.02	$\frac{45.74}{18.02} = 2.539$
Total.	99.95		

The atomic ratios of potassium and aluminium being nearly equal, one atom of each of these elements will be present with two sulphuric acid radicles and twelve molecules of water, since their atomic ratios are respectively twice and twelve times as great as that of potassium, giving the formula $KAl(SO_4)_2 \cdot 12H_2O$.

751. Many Minerals are found in the form of sharply defined homogeneous crystals, which contain varying amounts of several elements. These minerals contain several salts which crystallize in the same system, and are therefore called isomorphous. Dolomite is an example of such a mineral, in which varying amounts of magnesium and calcium carbonates are present. Small amounts of iron, aluminium, and silica are also present. The silicic acid is able to replace a portion of the carbonic acid forming calcium or magnesium silicates, while the iron and aluminium are able to replace a portion of the calcium and magnesium forming carbonates or silicates. A general formula, $M''RO_3$, will express the composition of the mineral. M'' represents the bivalent bases, calcium, magnesium, ferrous iron, or even two valences of an aluminium atom. R represents the carbon or silicon.

The method of obtaining the formula from an analysis is shown by the following analysis of dolomite:

Per cent of CO_2	46.80	$\frac{46.80}{44.0} = 1.064$
“ “ “ SiO_2	.62	$\frac{.62}{60.4} = .010$
Total acid equivalents, $R''O_2 = 1.074$		—
“ “ “ FeO	.21	$\frac{.21}{71.09} = .003$
“ “ “ CaO	32.35	$\frac{32.35}{56.1} = .577$
“ “ “ MgO	19.83	$\frac{19.83}{40.36} = .491$
Total	99.81	—
Total basic equivalents, $M''O = 1.071$		
Ratio of acids to bases =		$\frac{1.074}{1.071} = 1.003$

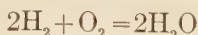
The formula of the dolomite will therefore be $\text{MgCO}_3, \text{CaCO}_3$, small amounts of the base being replaced by FeO , and a little of the acid by SiO_2 .

For each atom of bivalent metal there is present one acid radicle, the number 1.003 being so close to 1.000 that the difference may be ascribed to the unavoidable experimental errors of the analysis. Ratios as high as 1.02 or even 1.03 may be produced by errors which occur in fairly good analytical work, although the analytical worker should not be satisfied unless the ratio is usually less than 1.01.

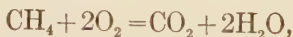
BALANCING OF EQUATIONS.

The calculation of nearly all volumetric determinations is based on the chemical equation which represents the reaction taking place. While it is true that the chemical equation is the expression of a quantitative analysis and should not be written unless the quantitative analysis has first been made, this view of the matter is taken only by the research chemist. In ordinary analytical work the correctness of the equation is assumed, and the quantitative result is calculated from it. The equation must therefore be written before the calculation is made.

752. The Simple Synthetical Equation, such as

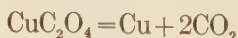


or

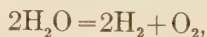


is required mainly for gas analysis.

753. The Analytical Equations, such as



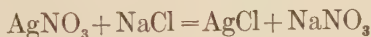
or



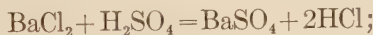
are most commonly required to express electrical decompositions. When the elements or compounds produced by the reaction are known, the equations are balanced by counting the number of atoms of each element on each side of the equation. For example, in the second equation given, the molecule of methane requires for its oxidation two atoms of oxygen for the carbon atom and two atoms for the four hydrogen atoms. The first member will

therefore contain C . . . 1, H . . . 4, and O . . . 4, while the second member will contain C . . . 1, H . . . 4, and O . . . 4. These numbers being identical for each element, the equation is balanced.

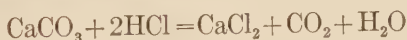
754. Metathetical Equations are far more commonly met with, as they represent the two types of chemical reaction which are most commonly carried out; namely (a) those involving the production of a precipitate when two substances in solution are brought together, such as



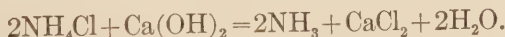
or



(b) those involving the production of a substance which is in the gaseous form under the conditions of the experiment, as



or

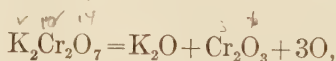


Equations such as these may be balanced by adding or subtracting molecules of one or the other substance until the number of atoms of each element is identical in each member of the equation. It is far better, however, to take into consideration the fact that some of the elements are combined into groups or radicles which do not separate into their constituent atoms. NO_3 is such a radicle, and in the first equation given the number of NO_3 radicles on each side of the equation must be identical. SO_4 acts as a radicle in the same manner. In the third equation the carbon remains combined with two atoms of oxygen as CO_2 , and two molecules of hydrochloric acid must be introduced, because one atom of calcium requires two atoms of chlorine to form calcium chloride, while the two atoms of hydrogen unite with the remaining atoms of oxygen in the calcium carbonate. In a similar manner the ammonia radicle NH_3 is considered as a unit in the fourth equation.

755. Oxidation and Reduction Equations are more difficult to balance since two distinct reactions generally take place. The

valence of two substances changes, involving the transference of oxygen or its equivalent, and in the second place an acid or an alkali reacts with some of the elements present to form salts. In balancing these equations the oxidizing and reducing substances must first be introduced in equivalent amounts. Then the amount of acid or base necessary to combine with the bases or acid liberated by the first reaction must be introduced.

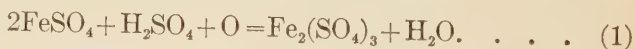
In order to balance the oxidizing and reducing equations the amount of oxygen absorbed or liberated must be known for each substance present. For instance, a molecule of potassium dichromate breaks up as follows:



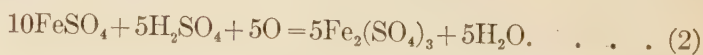
liberating three atoms of oxygen. Potassium permanganate breaks up so as to give five atoms of oxygen for every two molecules of the salt, as follows:



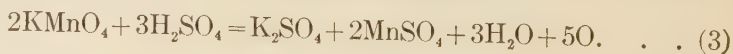
Amongst reducing substances two atoms of ferrous iron take up one atom of oxygen to form ferric iron while one atom of stannous tin takes up one atom of oxygen or its equivalent. Two molecules of potassium permanganate giving five atoms of oxygen are therefore able to oxidize ten atoms of ferrous iron. If the iron is present as ferrous sulphate one molecule of sulphuric acid will be required to convert two atoms of ferrous iron into ferric iron as follows:



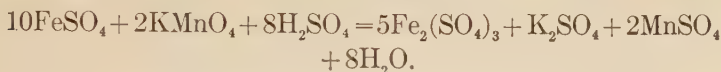
As five atoms of oxygen are given by the two molecules of potassium permanganate we must multiply each member of the equation by five, giving:



The potassium and manganese of the potassium permanganate are also converted into sulphates, two molecules of potassium permanganate requiring three molecules of sulphuric acid as follows:



Combining equation (2) and (3), we obtain the complete equation

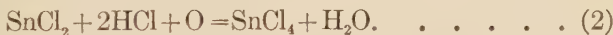


The free oxygen disappears from both equations since it is present in the first member in the potassium permanganate and in the second as water.

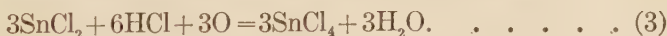
The oxidation of stannous chloride with potassium dichromate can also be written in two equations which may then be combined into one. The potassium dichromate liberates oxygen in the presence of . reducing agent according to the following equation:



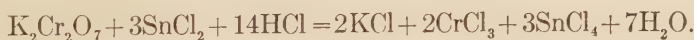
The stannous chloride in the presence of acid and an oxidizing agent reacts as follows:



As one molecule of potassium dichromate liberates three atoms of oxygen equation (2) must be multiplied by three, giving:



By combining equations (1) and (3) we obtain the complete equation as follows:

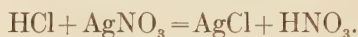


CALCULATION OF VOLUMETRIC DETERMINATIONS.

As volumetric solutions are generally made on the normal basis of strength the calculation of the results is quite simple. Roundabout and very cumbersome methods of calculation are nevertheless often used.

756. Standard Solutions.—When solutions such as hydrochloric or sulphuric acid have been standardized by weighing precipitates of silver chloride or barium sulphate the weight of the acid radicle present in the precipitate may be computed. From this weight the corresponding weight of acid may be computed, and finally the ratio of this weight to the theoretical weight for a normal solution may be calculated. The same

result may, however, be obtained by a single calculation. As a liter of normal hydrochloric acid contains the gram molecular weight of the acid it must give a gram molecular weight of silver chloride according to the equation,



If 10 c.c. of the acid has been taken for the determination the silver chloride precipitate should weigh 1.4338 or 1/100th of the gram molecular weight. The ratio of this number to the weight found will give the strength of the acid in terms of normal. For example, if 1.6728 grams of AgCl were obtained, the acid is $1.1667\text{N} \left(\frac{1.6728}{1.4338} \right)$. To dilute the acid to exact strength there must be added 166.7 c.c. of water to one liter of the acid. If the inverse ratio is taken $\left(\frac{1.4338}{1.6728} \right)$, the number .85712 is obtained and the dilution must be made by diluting 857.12 c.c. of the strong acid to one liter.

757. Acidimetry and Alkalimetry.—Having obtained a normal acid solution the calculation of the amount of any substance titrated is equally simple. For all univalent bases titrated one liter of the acid is equal to the gram molecular weight of the base. For example, one liter of a normal acid, whether it is sulphuric or hydrochloric, is equal to 17.034 grams of ammonia, while one c.c. is equal to one-thousandth of this amount or .017034 gram. If 10 c.c. of acid has been used to titrate a given amount of ammonia, there is present .17034 gram of NH_3 . If this ammonia has been formed from the nitrogen contained in a substance analyzed, the amount of nitrogen may be computed directly, since one liter of a normal acid will be equivalent to 14.01 grams of nitrogen in the form of ammonia. If, for example, the ammonia has been obtained from an ammonium salt, such as ammonium sulphate, the value of the normal acid in terms of this salt is obtained from its molecular weight, half of which is taken since each molecule contains two molecules of ammonia.

The value of a standard acid in terms of a given salt will sometimes vary with the indicator used, as already explained in Chapter XX, page 250. If disodic phosphate is titrated with a strong

acid, using methyl orange as the indicator, the following reaction will take place:



A liter of normal acid will therefore be equal to a gram molecular weight of disodic phosphate which will be 358.54 grams of the crystallized salt. While the disodic phosphate is alkaline to methyl orange it is neutral to phenolphthalein, to which the trisodium salt is alkaline. If the latter salt is titrated with acid, using phenolphthalein as the indicator, the following reaction takes place:



One liter of a normal acid is therefore equal to the gram molecular weight of this salt or 386.54 grams of the crystallized salt. A mixture of trisodic and disodic phosphates may therefore be analyzed by titration with a standard acid, using phenolphthalein and methyl orange as the indicators. The method of calculation is seen from the following illustration: One gram of a sample of disodic phosphate was titrated with fifth-normal acid. With phenolphthalein 1.50 c.c. of acid were used, and when methyl orange had been added 13.5 c.c. acid were required to again give the acid reaction. The acid used with the phenolphthalein represents the amount of trisodic phosphate present, 1 c.c. of fifth-normal acid being equal to .07608 gram of this salt.

$$\text{Percentage of Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O} = \frac{1.50 \times .07608}{1.000} = 11.41.$$

The 13.50 c.c. of acid used with the methyl orange neutralized the disodic phosphate present in the original material and that produced by the titration with phenolphthalein. The acid used for the latter purpose will be exactly equal to that used with the phenolphthalein, in this case 1.50 c.c. The acid necessary to neutralize the disodic phosphate originally present will be 12.00 c.c. (13.50 - 1.50). The percentage of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ will be

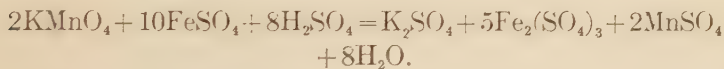
$$\frac{12.00 \times .0717}{1.000} = 86.04$$

758. Percentage Given by Number of Cubic Centimeters of Acid Used.—Frequently it is convenient to use a solution of such a strength that when a given weight of substance is taken the number of cubic centimeters used in the titration shall be equal to the percentage of a given constituent. For this purpose the solution must be made of such a strength that 100 c.c. are equal to the amount of substance to be weighed out, *provided the substance is absolutely pure*. If sodium carbonate is the substance to be titrated and one gram is the amount to be weighed out, 100 c.c. of the acid must be equal to 1 gram of pure sodium carbonate. As 100 c.c. of a normal acid are equal to 5.3 grams of sodium carbonate, the acid required must be $\frac{1}{5.3}$ rd normal. If an acid double this strength is used the number of cubic centimeters used must be multiplied by 2 to give the percentage. The amount of substance to be weighed out may also be so chosen that the percentage shall be equal to the number of cubic centimeters used in a titration. The acid may then be of any desired strength. The amount of substance weighed out must in every case be equal to the weight of the pure substance, which will just neutralize 100 c.c. of the acid. In the case of a fifth-normal acid 100 c.c. are equal to 1.06 grams of pure sodium carbonate. If this amount of the impure article be weighed out and titrated with the acid the number of cubic centimeters used will be equal to the percentage of Na_2CO_3 present. This is evident from the consideration that while 1.06 grams of the pure compound will require 100 c.c., any decrease in the purity of the substance will produce a proportionate decrease in the amount of acid used in its titration.

759. Oxidation and Reduction Titrations.—In calculating the results obtained by means of oxidizing and reducing solutions the amount of oxygen absorbed or liberated by the substances acted upon must always be kept in mind. Equivalent weights of reducing or oxidizing substances absorb or give up the same amount of oxygen. It has already been shown that 31.63 grams of KMnO_4 contain the same amount (8 grams) of available oxygen as 49.05 grams of $\text{K}_2\text{Cr}_2\text{O}_7$. A liter of solution containing either of these amounts of oxidizing substances is a normal solution. 126.97 grams of iodine liberate the same amount of oxygen to

reducing substances, and dissolved in a liter give a normal oxidizing solution. These different amounts of oxidizing substances are therefore equal to each other, because the same amount of free oxygen is furnished by each.

The method of shortening calculations by applying this principle may be seen from the following examples: A potassium permanganate solution which had been standardized by means of pure iron wire was used to standardize a sodium thiosulphate solution. The standardization of the potassium permanganate solution with iron takes place according to the following equation:



Two molecules of potassium permanganate are therefore equal to ten atoms of iron. A measured volume of the permanganate solution was acidified with hydrochloric acid after the addition of potassium iodide. Iodine was liberated according to the following equation:

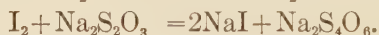
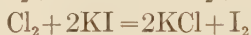


The iodine liberated is then titrated with sodium thiosulphate solution. By this equation two molecules of potassium permanganate are equal to ten atoms of iodine. As by the first equation the same amount of potassium permanganate is equal to ten atoms of iron, one atom of iron is equal to one atom of iodine; that is, 55.9 parts of iron are equal to 126.85 parts of iodine. As 1 c.c. of the potassium permanganate solution was found equal to .01115 gram of iron the value of 1 c.c. in iodine is obtained from the following proportion:

$$55.9 : 126.85 :: .01115 : x \\ x = .0253 \text{ gram.}$$

As 25 c.c. of the potassium permanganate solution required 23 c.c. of the thiosulphate solution to titrate the iodine liberated, the iodine value of 1 c.c. of the latter solution is equal to $\frac{25 \times .0253}{23}$, or .0275 gram.

760. Iodometric Titrations.—In a similar manner the value of the thiosulphate solution in terms of any substance it may be used to titrate may be calculated. The intermediate reactions are used simply to find the number of iodine atoms equivalent to one molecule of the substance titrated. For example, manganese dioxide may be boiled with hydrochloric acid, the chlorine evolved being absorbed in potassium iodide, and the iodine liberated titrated with the thiosulphate solution. The following reactions take place:



One molecule of manganese dioxide is therefore equal to two atoms of iodine. The value of 1 c.c. of the sodium thiosulphate solution in terms of manganese dioxide is obtained from the following proportion:

$$\begin{array}{l} \text{I}_2 : \text{MnO}_2 :: .0275 : x \\ 253.7 : 87 :: .0275 : x \\ x = .00943 \end{array}$$

APPENDIX.

REAGENTS.

It is important that the reagents used should be of known definite strength and that the strength should be indicated on the bottles. So far as possible also the reagents should be of *uniform* strength. This is not always possible on account of the solubilities of the salts employed. The strength is most easily indicated by the normal system of nomenclature. Chemically pure material should always be used. The impurities which may be present and the tests to be applied are given in the notes on pp. 32-35. Many salts when in solution, especially those that react alkaline, act on the glass becoming contaminated with silica and other constituents of the glass. Only recently prepared solutions of such reagents should be used. It is therefore advisable to keep the dry salts at hand and make up the solutions only as required for immediate use.

REAGENTS OF FIVE TIMES NORMAL STRENGTH. LABEL, 5 N.

Sulphuric Acid, H_2SO_4Equivalent = 49

Ordinary concentrated acid, sp. gr. 1.84, has a strength thirty-six times normal, and may be designated 36 N. One volume of strong acid diluted with 6 volumes of water = 5 N.

Nitric Acid, HNO_3Equivalent = 63

Concentrated acid, sp. gr. 1.40 = 15 N. One volume of strong acid diluted with 2 volumes of water = 5 N.

Hydrochloric Acid, HClEquivalent = 36.5

Concentrated acid, sp. gr. 1.20 = 13 N. Five volumes of strong acid diluted with 8 volumes of water = 5 N.

Acetic Acid, $\text{H.C}_2\text{H}_3\text{O}_2$ Equivalent = 60
 Glacial acid, M.P. 10°C. , = 17 N. One volume of glacial acid diluted with $2\frac{1}{2}$ volumes of water = 5 N.

Potassium Hydroxide, KOH Equivalent = 56
 280 grams dissolved in water and diluted to one liter = 5 N.

Sodium Hydroxide, NaOH Equivalent = 40
 200 grams dissolved in water and diluted to one liter = 5 N.

Ammonia (solution in water, NH_4OH). Equivalent = 35
 The strong solution, sp. gr. 0.90 = 15 N. One volume of the strong solution diluted with 2 volumes of water = 5 N.

Ammonium Sulphide, $(\text{NH}_4)_2\text{S}$ Equivalent = 34
 600 c.c. of 5 N ammonia are saturated with sulphuretted hydrogen; this gives hydrogen ammonium sulphide, NH_4HS . This is made up to 1 liter by adding 5 N ammonia. (This reagent is slowly decomposed by atmospheric oxygen, ammonia is evolved, and yellow ammonium sulphide, $(\text{NH}_4)_2\text{S}_2$, is formed.)

Sodium Sulphide, Na_2S Equivalent = 39
 200 grams of sodium hydroxide are dissolved in 800 c.c. of water. 400 c.c. of this solution are saturated with sulphuretted hydrogen and the remaining half added, together with water sufficient to make the volume up to 1 liter. When hydrogen sodium sulphide, NaHS , is required, the sodium hydroxide is simply saturated with sulphuretted hydrogen, without the further addition of sodium hydroxide.

Ammonium Chloride, NH_4Cl Equivalent = 53.5
 267.5 grams of the salt dissolved in water and diluted to one liter = 5 N.

Ammonium Carbonate, $(\text{NH}_4)_2\text{CO}_3$ Equivalent = 48
 200 grams of ammonium sesquicarbonate (commercial carbonate) dissolved in 350 c.c. of 5 N ammonia, and diluted with water to one liter = 5 N.

Ammonium Acetate, $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ Equivalent = 77
 To 300 c.c. of glacial acetic acid (17 N) an equal volume of water is added, the acid neutralized with strong ammonia and diluted to one liter = 5 N.

REAGENTS OF NORMAL STRENGTH. LABEL, N.

The following normal reagents are prepared by dissolving the equivalent weight in grams of the various salts in water, and diluting to one liter. In all cases the nearest whole number to the equivalent weight may be taken as sufficiently exact.

Barium chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	Equivalent weight	122.0
Disodium phosphate, $\text{HN}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$. “ “		119.3
Lead acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ “ “		189.5
“Magnesia mixture” (MgCl_2 , $(\text{NH}_4\text{Cl})_2$, and NH_4OH).		

68 grams of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, together with 165 grams of ammonium chloride, are dissolved in 300 c.c. of water; 300 c.c. of 5 N ammonia are added, and the solution diluted with water to one liter.

Stannous chloride, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ Equivalent weight 112.5

112 grams of the salt are dissolved in 200 c.c. of 5 N hydrochloric acid and the solution diluted with water to one liter. Fragments of granulated tin should be placed in the solution.

REAGENTS OF VARIOUS STRENGTHS.

Ammonium oxalate, $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. Equivalent weight 80.0

40 grams dissolved in one liter = $\frac{\text{N}}{2}$ solution.

Molybdate Solution.—The molybdate solution is made as follows: 75 grams of ammonium molybdate are dissolved in 500 c.c. of water with the addition of a little ammonia if necessary. If still turbid, the solution is filtered and then poured with constant stirring into 500 c.c. of a mixture of 250 c.c. of concentrated nitric acid (sp. gr. 1.40) and 250 c.c. of water. The solution may also be made from molybdic oxide by dissolving 60 grams in 440 c.c. of water and 60 c.c. strong ammonia (sp. gr. 0.90), and pouring the solution into 500 c.c. of nitric acid diluted as already directed. The freshly made molybdate solution must be allowed to stand in a warm place for several days. The clear solution is decanted or filtered off for use. Large amounts of the solution should not be

made up at one time, since it will not keep more than several months, as the molybdic acid is slowly precipitated.

Mercuric chloride, HgCl_2 Equivalent weight 135.5

27 grams dissolved in one liter = $\frac{N}{5}$ solution.

Silver nitrate, AgNO_3 Equivalent weight 170.0

3.4 grams dissolved in 100 c.c. = $\frac{N}{5}$ solution.

Potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$ Equivalent weight 294.5

100 grams are dissolved in one liter of water.

TABLE I. INTERNATIONAL ATOMIC WEIGHTS
FOR 1909*

O = 16

Name.	Symbol.	Atomic Weight.	Name.	Symbol.	Atomic Weight.
Aluminium.....	Al	27.1	Molybdenum.....	Mo	96.0
Antimony.....	Sb	120.2	Neodymium.....	Nd	144.3
Argon.....	A	39.9	Neon.....	Ne	20.0
Arsenic.....	As	75.0	Nickel.....	Ni	58.68
Barium.....	Ba	137.37	Nitrogen.....	N	14.01
Bismuth.....	Bi	208.0	Osmium.....	Os	190.9
Boron.....	B	11.0	Oxygen.....	O	16.00
Bromine.....	Br	79.92	Palladium.....	Pd	106.71
Cadmium.....	Cd	112.40	Phosphorus.....	P	31.0
Caesium.....	Cs	132.81	Platinum.....	Pt	195.0
Calcium.....	Ca	40.09	Potassium.....	K	39.10
Carbon.....	C	12.00	Praseodymium.....	Pr	140.6
Cerium.....	Ce	140.25	Radium.....	Ra	226.4
Chlorine.....	Cl	35.46	Rhodium.....	Rh	102.9
Chromium.....	Cr	52.1	Rubidium.....	Rb	85.45
Cobalt.....	Co	58.97	Ruthenium.....	Ru	101.7
Columbium.....	Cb	93.5	Samarium.....	Sm	150.4
Copper.....	Cu	63.57	Scandium.....	Sc	44.1
Dysprosium.....	Dy	162.5	Selenium.....	Se	79.2
Erbium.....	Er	167.4	Silicon.....	Si	28.3
Europium.....	Eu	152.0	Silver.....	Ag	107.88
Fluorine.....	F	19.0	Sodium.....	Na	23.00
Gadolinium.....	Gd	157.3	Strontium.....	Sr	87.62
Gallium.....	Ga	69.9	Sulphur.....	S	32.07
Germanium.....	Ge	72.5	Tantalum.....	Ta	181.0
Glucinum.....	Gl	9.1	Tellurium.....	Te	127.5
Gold.....	Au	197.2	Terbium.....	Tb	159.2
Helium.....	He	4.0	Thallium.....	Tl	204.0
Hydrogen.....	H	1.008	Thorium.....	Th	232.42
Indium.....	In	114.8	Thulium.....	Tm	168.5
Iodine.....	I	126.92	Tin.....	Sn	119.0
Iridium.....	Ir	193.1	Titanium.....	Ti	48.1
Iron.....	Fe	55.85	Tungsten.....	W	184
Krypton.....	Kr	81.8	Uranium.....	U	238.5
Lanthanum.....	La	139.0	Vanadium.....	V	51.2
Lead.....	Pb	207.10	Xenon.....	Xe	128
Lithium.....	Li	7.00	Ytterbium.....	Yb	172.0
Lutecium.....	Lu	174.0	(Neoytterbium).		
Magnesium.....	Mg	24.32	Yttrium.....	Yt	89.0
Manganese.....	Mn	54.93	Zinc.....	Zn	65.37
Mercury.....	Hg	200.0	Zirconium.....	Zr	90.6

* Compiled by the International Committee on Atomic Weights consisting of F. W. Clarke, W. Ostwald, T. E. Thorpe, and G. Urbain.

TABLE II.—CHEMICAL FACTORS AND THEIR LOGARITHMS.

	Atomic Weight.	Weighed.	Required	Factor.	
				Per Cent.	Logarithms.*
Aluminium	27.1	Al_2O_3	Al	53.03	9.72455
		AlPO_4	Al	22.20	9.34625
		"	Al_2O_3	41.85	9.62170
Antimony	120.2	Sb_2O_3	Sb	78.97	9.89749
Arsenic	75.0	As_2S_3	As	60.92	9.78478
		"	As_2O_3	80.42	9.90536
		$\text{Mg}_2\text{As}_2\text{O}_7$	As	48.29	9.68383
Barium	137.37	"	As_2O_3	63.74	9.80441
		"	As_2O_5	74.04	9.86947
		BaSO_4	Ba	58.85	9.76975
		"	BaCl_2	89.23	9.95054
		"	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	104.66	0.01982
		"	BaO	65.71	9.81760
		BaCO_3	Ba	69.61	9.84261
		"	BaO	77.71	9.89046
		"	C	06.08	8.78390
		"	CO_2	22.29	9.34817
		BaCrO_4	Ba	54.20	9.73396
		"	BaO	60.51	9.78181
Bismuth	208.0	Bi_2O_3	Bi	89.65	9.95257
		BiOCl	Bi	80.17	9.90399
		"	Bi_2O_3	89.42	9.95142
Bromine	79.92	AgBr	Br	42.56	9.62896
Cadmium	112.40	"	HBr	43.11	9.63461
		CdO	Cd	87.54	9.94220
		CdS	Cd	77.80	9.89099
Calcium	40.09	"	CdO	88.88	9.94879
		CaO	Ca	71.47	9.85415
		"	CaCO_3	178.44	0.25150
		CaCO_3	Ca	40.06	9.00265
		"	CaO	56.04	9.74850
		CaSO_4	Ca	29.44	9.46899
Carbon	12.00	"	CaO	41.20	9.61484
		CO_2	C	27.27	9.43573
		"	C	27.27	9.43573
Chlorine	35.46	AgCl	Cl	24.74	9.39337
		"	HCl	25.44	9.40543
		Ag	Cl	32.87	9.51680
Chromium	52.1	"	HCl	33.80	9.52886
		Cr_2O_3	Cr	68.46	9.83546
		"	CrO_3	131.54	0.11905
		"	CrO_4	152.57	0.18345
		PbCrO_4	Cr	16.12	9.20737
		"	CrO_3	30.97	9.49096
		"	CrO_4	35.92	9.55536
		"	Cr_2O_3	23.55	9.37191
		BaCrO_4	Cr	20.55	9.31291
		"	CrO_3	39.49	9.59650
		"	CrO_4	45.80	9.66090
		"	Cr_2O_3	30.02	9.47745
Cobalt	58.97	Co	CoO	127.14	0.10426
		CoSO_4	Co	38.04	9.58019
		"	CoO	48.36	9.68445
		$2\text{CoSO}_4 \cdot 3\text{K}_2\text{SO}_4$	Co	14.16	9.15107
Copper	63.57	"	CoO	18.00	9.25534
		Cu	CuO	125.17	0.09750
		"	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	392.83	0.59420

* The -10 after each of the logarithms has been omitted.

CHEMICAL FACTORS AND THEIR LOGARITHMS—(Continued).

	Atomic Weight.	Weighed.	Required.	Factor.	
				Per Cent.	Logarithms.
		CuO	Cu	79.89	9.90250
		Cu ₂ S	Cu	79.86	9.90232
		"	CuO	99.96	9.99981
		CuCNS	Cu	52.26	9.71814
		"	CuO	65.41	9.81564
Fluorine.....	19.0	CaF ₂	F	48.66	9.68718
		"	HF	51.24	9.70964
Hydrogen.....	1.008	H ₂ O	H	11.19	9.04884
Iodine.....	126.92	AgI	I	54.06	9.73283
		"	HI	54.48	9.73627
		PdI ₂	HI	70.97	9.85704
		"	I	70.40	9.84760
Iron.....	55.85	Fe ₂ O ₃	Fe	69.94	9.84475
		"	FeO	89.98	9.95416
		FePO ₄	Fe	37.02	9.56848
		"	FeO	47.63	9.67789
Lead.....	207.10	PbO	Pb	92.83	9.96768
		PbO ₂	Pb	86.62	9.93760
		PbS	Pb	86.59	9.93747
		"	PbO	93.28	9.96979
		PbSO ₄	Pb	68.31	9.83449
		"	PbO	73.59	9.86681
		PbCl ₂	Pb	74.49	9.87211
		"	PbO	80.25	9.90443
		PbCrO ₄	Pb	64.08	9.80671
		"	PbO	69.03	9.83903
Magnesium...	24.32	MgO	Mg	60.32	9.78044
		Mg ₂ P ₂ O ₇	Mg	21.85	9.33938
		"	MgO	36.22	9.55894
		MgSO ₄	Mg	20.20	9.30538
		"	MgO	33.49	9.52493
Manganese.....	54.93	Mn ₂ O ₄	Mn	72.03	9.85749
		"	MnO	93.01	9.96851
		"	MnO ₂	113.98	0.05685
		MnS	Mn	63.14	9.80029
		"	MnO	81.53	9.91131
		Mn ₂ P ₂ O ₇	Mn	38.70	9.58774
		"	MnO	49.98	9.69876
		MnSO ₄	Mn	36.38	9.56083
		"	MnO	46.97	9.67185
Mercury.....	200.0	Hg	HgO	108.00	0.03342
		HgS	Hg	86.18	9.93541
		"	HgCl ₂	116.74	0.06722
		"	HgO	93.07	9.96883
		HgCl	Hg	84.94	9.92911
		"	HgO	91.73	9.96253
Nickel.....	58.68	Ni	NiO	127.26	9.10471
		NiO	Ni	78.58	9.89529
		NiSO ₄	Ni	37.92	9.57886
		"	NiO	48.26	9.68357
Nitrogen.....	14.01	(NH ₄) ₂ PtCl ₆	N	6.31	8.80024
		"	NH ₃	7.68	8.88514
		"	NH ₄	8.13	8.91004
		C ₂₀ H ₁₆ N ₄ .HNO ₃	HNO ₃	15.47	9.18952
		"	N ₂ O ₅	12.87	9.10958

CHEMICAL FACTORS AND THEIR LOGARITHMS—(Continued).

	Atomic Weight.	Weighed.	Required.	Factor.	
				Per cent.	Logarithms.*
Platinum	195.0	Pt	N	14.37	9.15744
		"	NH ₃	17.47	9.24234
		"	NH ₄	18.50	9.26724
Phosphorus	31.0	Mg ₂ P ₂ O ₇	P	27.85	9.44478
		"	PO ₄	85.34	9.93114
		"	P ₂ O ₅	63.78	9.80468
Molybdenum ...	96.0	(NH ₄) ₃ PO ₄ .12MoO ₃	P	1.65	8.21787
		"	PO ₄	5.06	8.70423
		"	P ₂ O ₅	3.78	8.57777
Potassium.	39.10	KCl	K	52.44	9.71967
		"	K ₂ O	63.17	9.80051
		K ₂ PtCl ₆	K	16.09	9.20661
		"	K ₂ O	19.38	9.28745
		K ₂ SO ₄	K	44.87	9.65199
		"	K ₂ O	54.06	9.73283
Selenium	79.2	Se	SeO ₂	140.40	0.14737
Silicon.....	28.3	SiO ₂	Si	46.93	9.67147
Silver.....	107.88	AgCl	Ag	75.26	9.87657
		AgBr	Ag	57.44	9.75924
		AgI	Ag	45.95	9.66224
		Ag ₂ S	Ag	87.06	9.93982
Sodium.....	23.00	NaCl	Na	39.34	9.59487
		"	Na ₂ O	53.03	9.72451
		Na ₂ SO ₄	Na	32.38	9.51026
		"	Na ₂ O	43.64	9.63989
		Na ₂ CO ₃	Na	43.40	9.63745
		"	Na ₂ O	58.49	9.76708
Strontium.....	87.62	SrCO ₃	Sr	59.35	9.77345
		"	SrO	70.19	9.84629
		SrSO ₄	Sr	47.70	9.67852
		"	SrO	56.41	9.75136
Sulphur	32.07	BaSO ₄	S	13.74	9.13793
		"	SO ₂	27.45	9.43848
		"	SO ₃	34.30	9.53530
		"	SO ₄	41.16	9.61442
		"	H ₂ SO ₄	42.02	9.62345
Tellurium.....	127.5	Te	TeO ₂	125.09	0.09725
		Sn	SnO	113.44	0.05478
		"	SnO ₂	126.89	0.10343
Tin.....	119.0	SnO ₂	Sn	78.81	9.89657
Titanium	48.1	TiO ₂	Ti	60.05	9.77852
Zinc.....	65.37	ZnO	Zn	80.34	9.90492
		Zn ₂ P ₂ O ₇	Zn	42.90	9.63248
		"	ZnO	53.40	9.72756
		ZnS	Zn	67.00	9.82664
		"	ZnO	83.51	9.92172

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TABLES OF LOGARITHMS AND
ANTILOGARITHMS.

TABLE III.—LOGARITHMS.

Natural Numbers.											PROPORTIONAL PARTS.									
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9	
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37	
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34	
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31	
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29	
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27	
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25	
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24	
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22	
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21	
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20	
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19	
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18	
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17	
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17	
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16	
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15	
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15	
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14	
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14	
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13	
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13	
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12	
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12	
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12	
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11	
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11	
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11	
37	56 2	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10	
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10	
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10	
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10	
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9	
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9	
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9	
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9	
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9	
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8	
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8	
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8	
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8	
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8	
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8	
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7	
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7	
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7	

LOGARITHMS.

Natural Numbers.	0	1	2	3	4	5	6	7	8	9	PROPORTIONAL PARTS.								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7897	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	6	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	6	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	6	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	6	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	6	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	5	6	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	6
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	6
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	6
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	6
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	5	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	5	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	5	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	5	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	5	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	5	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	5	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	5	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	5	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	5	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	4	4

TABLE IV.—ANTILOGARITHMS.

Logarithms.											PROPORTIONAL PARTS.									
	0	1	2	3	4	5	6	7	8	9										
											1	2	3	4	5	6	7	8	9	
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2	
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2	
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2	
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2	
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2	
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2	
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2	
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2	
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3	
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3	
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3	
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3	
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3	
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3	
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3	
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3	
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3	
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3	
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3	
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3	
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3	
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3	
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3	
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4	
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4	
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4	
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	2	3	3	4	
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	2	3	3	4	
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	2	3	3	4	
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	2	3	3	4	
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	2	3	3	4	
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	2	3	3	4	
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	2	3	3	4	
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	2	3	3	4	
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	2	3	3	4	5	
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	2	3	3	4	5	
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	2	3	3	4	5	
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	2	3	3	4	5	
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	2	3	3	4	5	
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	2	3	3	4	5	
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	2	3	3	4	5	
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	2	3	3	4	5	
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	2	3	3	4	5	
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	2	2	3	3	4	5	
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	2	2	3	3	4	5	
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	2	2	3	3	4	5	
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	2	2	3	3	4	5	
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	2	2	3	3	4	5	
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	2	2	3	3	4	5	
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	2	2	3	3	4	5	

ANTILOGARITHMS.

Logarithms.											PROPORTIONAL PARTS.									
	0	1	2	3	4	5	6	7	8	9										
											1	2	3	4	5	6	7	8	9	
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7	
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7	
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7	
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7	
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7	
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7	
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8	
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8	
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8	
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8	
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8	
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9	
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9	
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9	
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9	
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9	
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10	
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10	
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10	
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10	
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11	
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11	
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	8	9	10	11	
.73	5370	5383	5395	5408	5420	5433	5445	5457	5470	5483	1	3	4	5	6	8	9	10	11	
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12	
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12	
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12	
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12	
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13	
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13	
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13	
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14	
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	1	14	
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14	
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	1	15	
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15	
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15	
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16	
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16	
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16	
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17	
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17	
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17	
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18	
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18	
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19	
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19	
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20	
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20	
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20	

TABLE V.—SPECIFIC GRAVITY OF AMMONIA SOLUTIONS AT 15° C.

LUNGE AND WIERNIK.*

Specific Gravity at 15° 4° in Vacuo.	Per Cent NH ₃ , Grams.	1 Liter Contains NH ₃ , Grams.	Correction of Specific Gravity for ± 1°.	Specific Gravity at 15° 4° in Vacuo.	Per Cent NH ₃ , Grams.	1 Liter Contains NH ₃ , Grams.	Correction of Specific Gravity for ± 1°.
1.000	0.00	0.0	0.00018	0.940	15.63	146.9	0.00039
0.998	0.45	4.5	0.00018	0.938	16.22	152.1	0.00040
0.996	0.91	9.1	0.00019	0.936	16.82	157.4	0.00041
0.994	1.37	13.6	0.00019	0.934	17.42	162.7	0.00041
0.992	1.84	18.2	0.00020	0.932	18.03	168.1	0.00042
0.990	2.31	22.9	0.00020	0.930	18.64	173.4	0.00042
0.988	2.80	27.7	0.00021	0.928	19.25	178.6	0.00043
0.986	3.30	32.5	0.00021	0.926	19.87	184.2	0.00044
0.984	3.80	37.4	0.00022	0.924	20.49	189.3	0.00045
0.982	4.30	42.2	0.00022	0.922	21.12	194.7	0.00046
0.980	4.80	47.0	0.00023	0.920	21.75	200.1	0.00047
0.978	5.30	51.8	0.00023	0.918	22.39	205.6	0.00048
0.976	5.80	56.6	0.00024	0.916	23.03	210.9	0.00049
0.974	6.30	61.4	0.00024	0.914	23.68	216.3	0.00050
0.972	6.80	66.1	0.00025	0.912	24.33	221.9	0.00051
0.970	7.31	70.9	0.00025	0.910	24.99	227.4	0.00052
0.968	7.82	75.7	0.00026	0.908	25.65	232.9	0.00053
0.966	8.33	80.5	0.00026	0.906	26.31	238.3	0.00054
0.964	8.84	85.2	0.00027	0.904	26.93	243.9	0.00055
0.962	9.35	89.9	0.00028	0.902	27.65	249.4	0.00056
0.960	9.91	95.1	0.00029	0.900	28.33	255.0	0.00057
0.958	10.47	100.3	0.00030	0.898	29.01	260.5	0.00058
0.956	11.03	105.4	0.00031	0.896	29.69	266.0	0.00059
0.954	11.60	110.7	0.00032	0.894	30.37	271.5	0.00060
0.952	12.17	115.9	0.00033	0.892	31.05	277.0	0.00060
0.950	12.74	121.0	0.00034	0.890	31.75	282.6	0.00061
0.948	13.31	126.2	0.00035	0.888	32.50	288.6	0.00062
0.946	13.88	131.3	0.00036	0.886	33.25	294.6	0.00063
0.944	14.46	136.5	0.00037	0.884	34.10	301.4	0.00064
0.942	15.04	141.7	0.00038	0.882	34.95	308.3	0.00065

* Zeit. f. angew. Chem., 1889, 181.

TABLE VI.—SPECIFIC GRAVITY OF HYDROCHLORIC ACID AT 15° C.

LUNGE AND MARCHLEWSKI.*

Specific Grav- ity at $\frac{15^\circ}{4^\circ}$ in Vacuo.	Degrees Baumé.†	Degrees Twaddell.	100 Parts by Weight Contain Grams, HCl.	1 Liter Contains in Kilograms, HCl.
1.000	0.0	0	0.16	0.0016
1.005	0.7	1	1.15	0.012
1.010	1.4	2	2.14	0.022
1.015	2.1	3	3.12	0.032
1.020	2.7	4	4.13	0.042
1.025	3.4	5	5.15	0.053
1.030	4.1	6	6.15	0.064
1.035	4.7	7	7.15	0.074
1.040	5.4	8	8.16	0.085
1.045	6.0	9	9.16	0.096
1.050	6.7	10	10.17	0.107
1.055	7.4	11	11.18	0.118
1.060	8.0	12	12.19	0.129
1.065	8.7	13	13.19	0.141
1.070	9.4	14	14.17	0.152
1.075	10.0	15	15.16	0.163
1.080	10.6	16	16.15	0.174
1.085	11.2	17	17.13	0.186
1.090	11.9	18	18.11	0.197
1.095	12.4	19	19.06	0.209
1.100	13.0	20	20.01	0.220
1.105	13.6	21	20.97	0.232
1.110	14.2	22	21.92	0.243
1.115	14.9	23	22.86	0.255
1.120	15.4	24	23.82	0.267
1.125	16.0	25	24.78	0.278
1.130	16.5	26	25.75	0.291
1.135	17.1	27	26.70	0.303
1.140	17.7	28	27.66	0.315
1.1425	18.0	..	28.14	0.322
1.145	18.3	29	28.61	0.328
1.150	18.8	30	29.57	0.340
1.152	19.0	..	29.95	0.345
1.155	19.3	31	30.55	0.353
1.160	19.8	32	31.52	0.366
1.163	20.0	..	32.10	0.373
1.165	20.3	33	32.49	0.379
1.170	20.9	34	33.46	0.392
1.171	21.0	..	33.65	0.394
1.175	21.4	35	34.42	0.404
1.180	22.0	36	35.39	0.418
1.185	22.5	37	36.31	0.430
1.190	23.0	38	37.23	0.443
1.195	23.5	39	38.16	0.456
1.200	24.0	40	39.11	0.469

* Zeit. angew. Chem., 1891, 135.

† For the American Standard Baumé scale and the specific-gravity table adopted by the Manufacturing Chemists' Association of the United States, see Van Nostrand's Chemical Annual.

TABLE VII.—SPECIFIC GRAVITY OF NITRIC ACID AT 15 °C.
LUNGE AND REY.*

Specific Gravity at 15° at 4° in Vacuo.	Degrees Baumé.†	Degrees Twaddell.	100 Parts by Weight Contain, Grams,		1 Liter Contains in Kilograms,	
			N ₂ O ₅ .	HNO ₃ .	N ₂ O ₅ .	HNO ₃ .
1.000	0	0	0.03	0.10	0.001	0.001
1.005	0.7	1	0.85	1.00	0.008	0.010
1.010	1.4	2	1.62	1.90	0.016	0.019
1.015	2.1	3	2.39	2.80	0.024	0.028
1.020	2.7	4	3.17	3.70	0.033	0.038
1.025	3.4	5	3.94	4.60	0.040	0.047
1.030	4.1	6	4.71	5.50	0.049	0.057
1.035	4.7	7	5.47	6.38	0.057	0.066
1.040	5.4	8	6.22	7.26	0.064	0.075
1.045	6.0	9	6.97	8.13	0.073	0.085
1.050	6.7	10	7.71	8.99	0.081	0.094
1.055	7.4	11	8.43	9.84	0.089	0.104
1.060	8.0	12	9.15	10.68	0.097	0.113
1.065	8.7	13	9.87	11.51	0.105	0.123
1.070	9.4	14	10.57	12.33	0.113	0.132
1.075	10.0	15	11.27	13.15	0.121	0.141
1.080	10.6	16	11.96	13.95	0.129	0.151
1.085	11.2	17	12.64	14.74	0.137	0.160
1.090	11.9	18	13.31	15.53	0.145	0.169
1.095	12.4	19	13.99	16.32	0.153	0.179
1.100	13.0	20	14.67	17.11	0.161	0.188
1.105	13.6	21	15.34	17.89	0.170	0.198
1.110	14.2	22	16.00	18.67	0.177	0.207
1.115	14.9	23	16.67	19.45	0.186	0.217
1.120	15.4	24	17.34	20.23	0.195	0.227
1.125	16.0	25	18.00	21.00	0.202	0.236
1.130	16.5	26	18.66	21.77	0.211	0.246
1.135	17.1	27	19.32	22.54	0.219	0.256
1.140	17.7	28	19.98	23.31	0.228	0.266
1.145	18.3	29	20.64	24.08	0.237	0.276
1.150	18.8	30	21.29	24.84	0.245	0.286
1.155	19.3	31	21.94	25.60	0.254	0.296
1.160	19.8	32	22.60	26.36	0.262	0.306
1.165	20.3	33	23.25	27.12	0.271	0.316
1.170	20.9	34	23.90	27.88	0.279	0.326
1.175	21.4	35	24.54	28.63	0.288	0.336
1.180	22.0	36	25.18	29.38	0.297	0.347
1.185	22.5	37	25.83	30.13	0.306	0.357
1.190	23.0	38	26.47	30.88	0.315	0.367
1.195	23.5	39	27.10	31.62	0.324	0.378
1.200	24.0	40	27.74	32.36	0.333	0.388
1.205	24.5	41	28.36	33.09	0.342	0.399
1.210	25.0	42	28.99	33.82	0.351	0.409
1.215	25.5	43	29.61	34.55	0.360	0.420
1.220	26.0	44	30.24	35.28	0.369	0.430
1.225	26.4	45	30.88	36.03	0.378	0.441
1.230	26.9	46	31.53	36.78	0.387	0.452
1.235	27.4	47	32.17	37.53	0.397	0.463
1.240	27.9	48	32.82	38.29	0.407	0.475
1.245	28.4	49	33.47	39.05	0.417	0.486
1.250	28.8	50	34.13	39.82	0.427	0.498

*Zeit. angew. Chem., 1891, 165.

† For the American Standard Baumé scale and the specific-gravity table adopted by the Manufacturing Chemists' Association of the United States, see Van Nostrand's Chemical Annual.

SPECIFIC GRAVITY OF NITRIC ACID AT 15° C.—(Continued).

Specific Gravity at 15° at 4° in Vacuo.	Degrees Baumé.	Degrees Twaddell.	100 Parts by Weight Contain, Grams,		1 Liter Contains in Kilograms,	
			N ₂ O ₅ .	HNO ₃ .	N ₂ O ₅ .	HNO ₃ .
1.255	29.3	51	34.78	40.58	0.437	0.509
1.260	29.7	52	35.44	41.34	0.447	0.521
1.265	30.2	53	36.09	42.10	0.457	0.533
1.270	30.6	54	36.75	42.87	0.467	0.544
1.275	31.1	55	37.41	43.64	0.477	0.556
1.280	31.5	56	38.07	44.41	0.487	0.568
1.285	32.0	57	38.73	45.18	0.498	0.581
1.290	32.4	58	39.39	45.95	0.508	0.593
1.295	32.8	59	40.05	46.72	0.519	0.605
1.300	33.3	60	40.71	47.49	0.529	0.617
1.305	33.7	61	41.37	48.26	0.540	0.630
1.310	34.2	62	42.06	49.07	0.551	0.643
1.315	34.6	63	42.76	49.89	0.562	0.656
1.320	35.0	64	43.47	50.71	0.573	0.669
1.325	35.4	65	44.17	51.53	0.585	0.683
1.330	35.8	66	44.89	52.37	0.597	0.697
1.3325	36.0	665	45.26	52.80	0.603	0.704
1.335	36.2	67	45.62	53.22	0.609	0.710
1.340	36.6	68	46.35	54.07	0.621	0.725
1.345	37.0	69	47.08	54.93	0.633	0.739
1.350	37.4	70	47.82	55.79	0.645	0.753
1.355	37.8	71	48.57	56.66	0.653	0.768
1.360	38.2	72	49.35	57.57	0.671	0.783
1.365	38.6	73	50.13	58.48	0.684	0.798
1.370	39.0	74	50.91	59.39	0.698	0.814
1.375	39.4	75	51.69	60.30	0.711	0.829
1.380	39.8	76	52.52	61.27	0.725	0.846
1.3833	40.0	..	53.08	61.92	0.735	0.857
1.385	40.1	77	53.35	62.24	0.739	0.862
1.390	40.5	78	54.20	63.23	0.753	0.879
1.395	40.8	79	55.07	64.25	0.768	0.896
1.400	41.2	80	55.97	65.30	0.783	0.914
1.405	41.6	81	56.92	66.40	0.800	0.933
1.410	42.0	82	57.86	67.50	0.816	0.952
1.415	42.3	83	58.83	68.63	0.832	0.971
1.420	42.7	84	59.83	69.80	0.849	0.991
1.425	43.1	85	60.84	70.98	0.867	1.011
1.430	43.4	86	61.86	72.17	0.885	1.032
1.435	43.8	87	62.91	73.39	0.903	1.053
1.440	44.1	88	64.01	74.68	0.921	1.075
1.445	44.4	89	65.13	75.98	0.941	1.098
1.450	44.8	90	66.24	77.28	0.961	1.121
1.455	45.1	91	67.38	78.60	0.981	1.144
1.460	45.4	92	68.56	79.98	1.001	1.168
1.465	45.8	93	69.79	81.42	1.023	1.193
1.470	46.1	94	71.06	82.90	1.045	1.219
1.475	46.4	95	72.39	84.45	1.068	1.246
1.480	46.8	96	73.76	86.05	1.092	1.274
1.485	47.1	97	75.18	87.70	1.116	1.302
1.490	47.4	98	76.80	89.60	1.144	1.335
1.495	47.8	99	78.52	91.60	1.174	1.369

SPECIFIC GRAVITY OF NITRIC ACID AT 15° C.—(Continued).

LUNGE AND REY.

Specific Gravity 15° at 4° in Vacuo	Degrees Baumé.	Degrees Twaddell.	100 Parts by Weight Contain, Grams,		1 Liter Contains in Kilograms,	
			N ₂ O ₅ .	HNO ₃ .	N ₂ O ₅ .	HNO ₃ .
1.500	48.1	100	80.65	94.09	1.210	1.411
1.501		...	81.09	94.60	1.217	1.420
1.502		...	81.50	95.03	1.224	1.428
1.503		...	81.91	95.55	1.231	1.436
1.504		...	82.29	96.00	1.238	1.444
1.505	48.4	101	82.63	96.39	1.244	1.451
1.506		...	82.94	96.76	1.249	1.457
1.507		...	83.26	97.13	1.255	1.464
1.508	48.5	...	83.53	97.50	1.260	1.470
1.509		...	83.87	97.84	1.265	1.476
1.510	48.7	102	84.09	98.10	1.270	1.481
1.511		...	84.23	98.32	1.274	1.486
1.512		...	84.46	98.53	1.277	1.490
1.513		...	84.63	98.73	1.280	1.494
1.514		...	84.78	98.90	1.283	1.497
1.515	49.0	103	84.92	99.07	1.287	1.501
1.516		...	85.04	99.21	1.29	1.504
1.517		...	85.15	99.34	1.292	1.507
1.518		...	85.26	99.46	1.294	1.510
1.519		...	85.35	99.57	1.296	1.512
1.520	49.4	104	85.44	99.67	1.299	1.515

TABLE VIII.—SPECIFIC GRAVITY OF SULPHURIC ACID.

LUNGE, ISLER, AND NAEF.*

Specific Gravity at 15° at 4° in Vacuo.	Degrees Baumé.†	Degrees Twaddell.	100 Parts by Weight Contain, Grams,		1 Liter Contains in Kilograms,	
			SO ₃ .	H ₂ SO ₄ .	SO ₃ .	H ₂ SO ₄ .
1.000	0	0	0.07	0.09	0.001	0.001
1.005	0.7	1	0.68	0.83	0.007	0.008
1.010	1.4	2	1.28	1.57	0.013	0.016
1.015	2.1	3	1.88	2.30	0.019	0.023
1.020	2.7	4	2.47	3.03	0.025	0.031
1.025	3.4	5	3.07	3.76	0.032	0.039
1.030	4.1	6	3.67	4.49	0.038	0.046
1.035	4.7	7	4.27	5.23	0.044	0.054
1.040	5.4	8	4.87	5.96	0.051	0.062
1.045	6.0	9	5.45	6.67	0.057	0.071
1.050	6.7	10	6.02	7.37	0.063	0.077
1.055	7.4	11	6.59	8.07	0.070	0.085
1.060	8.0	12	7.16	8.77	0.076	0.093
1.065	8.7	13	7.73	9.47	0.082	0.102
1.070	9.4	14	8.32	10.19	0.089	0.109
1.075	10.0	15	8.90	10.90	0.096	0.117
1.080	10.6	16	9.47	11.60	0.103	0.125
1.085	11.2	17	10.04	12.30	0.109	0.133
1.090	11.9	18	10.60	12.99	0.116	0.142
1.095	12.4	19	11.16	13.67	0.122	0.150
1.100	13.0	20	11.71	14.35	0.129	0.158
1.105	13.6	21	12.27	15.03	0.136	0.166
1.110	14.2	22	12.82	15.71	0.143	0.175
1.115	14.9	23	13.36	16.36	0.149	0.183
1.120	15.4	24	13.89	17.01	0.156	0.191
1.125	16.0	25	14.42	17.66	0.162	0.199
1.130	16.5	26	14.95	18.31	0.169	0.207
1.135	17.1	27	15.48	18.96	0.176	0.215
1.140	17.7	28	16.01	19.61	0.183	0.223
1.145	18.3	29	16.54	20.26	0.189	0.231
1.150	18.8	30	17.07	20.91	0.196	0.239
1.155	19.3	31	17.59	21.55	0.203	0.248
1.160	19.8	32	18.11	22.19	0.210	0.257
1.165	20.3	33	18.64	22.83	0.217	0.266
1.170	20.9	34	19.16	23.47	0.224	0.275
1.175	21.4	35	19.69	24.12	0.231	0.283
1.180	22.0	36	20.21	24.76	0.238	0.292
1.185	22.5	37	20.73	25.40	0.246	0.301
1.190	23.0	38	21.26	26.04	0.253	0.310
1.195	23.5	39	21.78	26.68	0.260	0.319
1.200	24.0	40	22.30	27.32	0.268	0.328
1.205	24.5	41	22.82	27.95	0.275	0.337
1.210	25.0	42	23.33	28.58	0.282	0.346
1.215	25.5	43	23.84	29.21	0.290	0.355
1.220	26.0	44	24.36	29.84	0.297	0.364
1.225	26.4	45	24.88	30.48	0.305	0.373
1.230	26.9	46	25.39	31.11	0.312	0.382
1.235	27.4	47	25.88	31.70	0.320	0.391
1.240	27.9	48	26.35	32.28	0.327	0.400
1.245	28.4	49	26.83	32.86	0.334	0.409
1.250	28.8	50	27.29	33.43	0.341	0.418
1.255	29.3	51	27.76	34.00	0.348	0.426
1.260	29.7	52	28.22	34.57	0.356	0.435

* Zeit. angew. Chem., 1890, 131; Chem. Ind., 1883, 39.

† For the American Standard Baumé scale and the specific-gravity table adopted by the Manufacturing Chemists' Association of the United States, see Van Nostrand's Chemical Annual.

SPECIFIC GRAVITY OF SULPHURIC ACID—(Continued).

Specific Gravity at 15° at 4° in Vacuo.	Degrees Baumé.	Degrees Twaddell.	100 Parts by Weight Contain, Grams,		1 Liter Contains in Kilograms,	
			SO ₃ .	H ₂ SO ₄ .	SO ₃ .	H ₂ SO ₄ .
1.265	30.2	53	28.69	35.14	0.363	0.444
1.270	30.6	54	29.15	35.71	0.370	0.454
1.275	31.1	55	29.62	36.29	0.377	0.462
1.280	31.5	56	30.10	36.87	0.385	0.472
1.285	32.0	57	30.57	37.45	0.393	0.481
1.290	32.4	58	31.04	38.03	0.400	0.490
1.295	32.8	59	31.52	38.61	0.408	0.500
1.300	33.3	60	31.99	39.19	0.416	0.510
1.305	33.7	61	32.46	39.77	0.424	0.519
1.310	34.2	62	32.94	40.35	0.432	0.529
1.315	34.6	63	33.41	40.93	0.439	0.538
1.320	35.0	64	33.88	41.50	0.447	0.548
1.325	35.4	65	34.35	42.08	0.455	0.557
1.330	35.8	66	34.80	42.66	0.462	0.567
1.335	36.2	67	35.27	43.20	0.471	0.577
1.340	36.6	68	35.71	43.74	0.479	0.586
1.345	37.0	69	36.14	44.28	0.486	0.596
1.350	37.4	70	36.58	44.82	0.494	0.605
1.355	37.8	71	37.02	45.35	0.502	0.614
1.360	38.2	72	37.45	45.88	0.509	0.624
1.365	38.6	73	37.89	46.41	0.517	0.633
1.370	39.0	74	38.32	46.94	0.525	0.643
1.375	39.4	75	38.75	47.47	0.533	0.653
1.380	39.8	76	39.18	48.00	0.541	0.662
1.385	40.1	77	39.62	48.53	0.549	0.672
1.390	40.5	78	40.05	49.06	0.557	0.682
1.395	40.8	79	40.48	49.59	0.564	0.692
1.400	41.2	80	40.91	50.11	0.573	0.702
1.405	41.6	81	41.33	50.63	0.581	0.711
1.410	42.0	82	41.76	51.15	0.589	0.721
1.415	42.3	83	42.17	51.66	0.597	0.730
1.420	42.7	84	42.57	52.15	0.604	0.740
1.425	43.1	85	42.96	52.63	0.612	0.750
1.430	43.4	86	43.36	53.11	0.620	0.759
1.435	43.8	87	43.75	53.59	0.628	0.769
1.440	44.1	88	44.14	54.07	0.636	0.779
1.445	44.4	89	44.53	54.55	0.643	0.789
1.450	44.8	90	44.92	55.03	0.651	0.798
1.455	45.1	91	45.31	55.50	0.659	0.808
1.460	45.4	92	45.69	55.97	0.667	0.817
1.465	45.8	93	46.07	56.43	0.675	0.827
1.470	46.1	94	46.45	56.90	0.683	0.837
1.475	46.4	95	46.83	57.37	0.691	0.846
1.480	46.8	96	47.21	57.83	0.699	0.856
1.485	47.1	97	47.57	58.28	0.707	0.865
1.490	47.4	98	47.95	58.74	0.715	0.876
1.495	47.8	99	48.34	59.22	0.723	0.885
1.500	48.1	100	48.73	59.70	0.731	0.896
1.505	48.4	101	49.12	60.18	0.739	0.906
1.510	48.7	102	49.51	60.65	0.748	0.916
1.515	49.0	103	49.89	61.12	0.756	0.926
1.520	49.4	104	50.28	61.59	0.764	0.936
1.525	49.7	105	50.66	62.06	0.773	0.946
1.530	50.0	106	51.04	62.53	0.781	0.957

SPECIFIC GRAVITY OF SULPHURIC ACID—(Continued).

Specific Gravity at $\frac{15^\circ}{4^\circ}$ in Vacuo.	Degrees Baumé.	Degrees Twaddell.	100 Parts by Weight Contain, Grams,		1 Liter Contains in Kilograms,	
			SO ₃ .	H ₂ SO ₄ .	SO ₃ .	H ₂ SO ₄ .
1.535	50.3	107	51.43	63.00	0.789	0.967
1.540	50.6	108	51.78	63.43	0.797	0.977
1.545	50.9	109	52.12	63.85	0.805	0.987
1.550	51.2	110	52.46	64.26	0.813	0.996
1.555	51.5	111	52.79	64.67	0.821	1.006
1.560	51.8	112	53.12	65.08	0.829	1.015
1.565	52.1	113	53.46	65.49	0.837	1.025
1.570	52.4	114	53.80	65.90	0.845	1.035
1.575	52.7	115	54.13	66.30	0.853	1.044
1.580	53.0	116	54.46	66.71	0.861	1.054
1.585	53.3	117	54.80	67.13	0.869	1.064
1.590	53.6	118	55.18	67.59	0.877	1.075
1.595	53.9	119	55.55	68.05	0.886	1.085
1.600	54.1	120	55.93	68.51	0.895	1.096
1.605	54.4	121	56.30	68.97	0.904	1.107
1.610	54.7	122	56.63	69.43	0.913	1.118
1.615	55.0	123	57.05	69.89	0.921	1.123
1.620	55.2	124	57.40	70.32	0.930	1.139
1.625	55.5	125	57.75	70.74	0.938	1.150
1.630	55.8	126	58.09	71.16	0.947	1.160
1.635	56.0	127	58.43	71.57	0.955	1.170
1.640	56.3	128	58.77	71.99	0.964	1.181
1.645	56.6	129	59.10	72.40	0.972	1.192
1.650	56.9	130	59.45	72.82	0.981	1.202
1.655	57.1	131	59.73	73.23	0.989	1.212
1.660	57.4	132	60.11	73.64	0.998	1.222
1.665	57.7	133	60.46	74.07	1.007	1.233
1.670	57.9	134	60.82	74.51	1.016	1.244
1.675	58.2	135	61.20	74.97	1.025	1.256
1.680	58.4	136	61.57	75.42	1.034	1.267
1.685	58.7	137	61.93	75.86	1.043	1.278
1.690	58.9	138	62.29	76.30	1.053	1.289
1.695	59.2	139	62.64	76.73	1.062	1.301
1.700	59.5	140	63.00	77.17	1.071	1.312
1.705	59.7	141	63.35	77.60	1.080	1.323
1.710	60.0	142	63.70	78.04	1.089	1.334
1.715	60.2	143	64.07	78.48	1.099	1.346
1.720	60.4	144	64.43	78.92	1.108	1.357
1.725	60.6	145	64.78	79.36	1.118	1.369
1.730	60.9	146	65.14	79.80	1.127	1.381
1.735	61.1	147	65.50	80.24	1.136	1.392
1.740	61.4	148	65.86	80.68	1.146	1.404
1.745	61.6	149	66.22	81.12	1.156	1.416
1.750	61.8	150	66.58	81.56	1.165	1.427
1.755	62.1	151	66.94	82.00	1.175	1.439
1.760	62.3	152	67.30	82.44	1.185	1.451
1.765	62.5	153	67.65	82.88	1.194	1.463
1.770	62.8	154	68.02	83.32	1.204	1.475
1.775	63.0	155	68.49	83.90	1.216	1.489
1.780	63.2	156	68.98	84.50	1.228	1.504
1.785	63.5	157	69.47	85.10	1.240	1.519
1.790	63.7	158	69.96	85.70	1.252	1.534
1.795	64.0	159	70.45	86.30	1.265	1.549
1.800	64.2	160	70.94	86.90	1.277	1.564

SPECIFIC GRAVITY OF SULPHURIC ACID—(Continued).

Specific Gravity at 15° 4° in Vacuo.	Degrees Baumé.	Degrees Twaddell.	100 Parts by Weight Contain, Grams,		1 Liter Contains in Kilograms,	
			SO ₃ .	H ₂ SO ₄ .	SO ₃ .	H ₂ SO ₄ .
1.805	64.4	161	71.50	87.60	1.291	1.581
1.810	64.6	162	72.08	88.30	1.305	1.598
1.815	64.8	163	72.69	89.05	1.319	1.621
1.820	65.0	164	73.51	90.05	1.338	1.639
1.821			73.63	90.20	1.341	1.643
1.822	65.1		73.80	90.40	1.345	1.647
1.823			73.96	90.60	1.348	1.651
1.824	65.2		74.12	90.80	1.352	1.656
1.825		165	74.29	91.00	1.356	1.661
1.826	65.3		74.49	91.25	1.360	1.666
1.827			74.69	91.50	1.364	1.671
1.828	65.4		74.86	91.70	1.368	1.676
1.829			75.03	91.90	1.372	1.681
1.830		166	75.19	92.10	1.376	1.685
1.831	65.5		75.35	92.30	1.380	1.690
1.832			75.53	92.52	1.384	1.695
1.833	65.6		75.72	92.75	1.388	1.700
1.834			75.96	93.05	1.393	1.706
1.835	65.7	167	76.27	93.43	1.400	1.713
1.836			76.57	93.80	1.406	1.722
1.837			76.90	94.20	1.412	1.730
1.838	65.8		77.23	94.60	1.419	1.739
1.839			77.55	95.00	1.426	1.748
1.840	65.9	168	78.04	95.60	1.436	1.759
1.8405			78.33	95.95	1.451	1.765
1.8410			79.19	97.00	1.458	1.786
1.8415			79.76	97.70	1.469	1.799
1.8410			80.16	98.20	1.476	1.808
1.8405			80.57	98.70	1.483	1.816
1.8400			80.98	99.20	1.490	1.825
1.8395			81.18	99.45	1.494	1.830
1.8390			81.39	99.70	1.497	1.834
1.8385			81.59	99.95	1.500	1.838

TABLE IX.—VAPOR TENSION OF WATER IN MILLIMETERS OF MERCURY.

MAGNUS.

Temp.	Millimeters.	Temp.	Millimeters.	Temp.	Millimeters.	Temp.	Millimeters.
0	4.525	8	7.964	15	12.677	23	20.909
+1	4.867	9	8.525	16	13.519	24	22.211
2	5.231	10	9.126	17	14.409	25	23.582
3	5.619	11	9.756	18	15.351	26	25.026
4	6.032	12	10.421	19	16.345	27	26.547
5	6.471	13	11.130	20	17.396	28	28.148
6	6.939	14	11.882	21	18.505	29	29.832
7	7.436			22	19.675	30	31.602

TABLE X.—DENSITY OF WATER.

ROSSETTI.

Tempera- ture.	Density (Density at 0°=1).	Volume (Volume at 0°=1).	Density (Density at 4°=1).	Volume (Volume at 4°=1).
-10	0.998274	1.001729	0.998145	1.001858
-9	0.998556	1.001449	0.998427	1.001575
-8	0.998814	1.001191	0.998685	1.001317
-7	0.999040	1.000963	0.998911	1.001089
-6	0.999247	1.000756	0.999118	1.000883
-5	0.999428	1.000573	0.999298	1.000702
-4	0.999584	1.000416	0.999455	1.000545
-3	0.999719	1.000281	0.999590	1.000410
-2	0.999832	1.000168	0.999703	1.000297
-1	0.999926	1.000074	0.999797	1.000203
0	1.000000	1.000000	0.999871	1.000129
+1	1.000057	0.999943	0.999928	1.000072
2	1.000098	0.999902	0.999969	1.000031
3	1.000120	0.999880	0.999991	1.000009
4	1.000129	0.999871	1.000000	1.000000
5	1.000119	0.999881	0.999990	1.000010
6	1.000099	0.999901	0.999970	1.000030
7	1.000062	0.999938	0.999933	1.000067
8	1.000015	0.999985	0.999886	1.000114
9	0.999953	1.000047	0.999824	1.000176
10	0.999876	1.000124	0.999747	1.000253
11	0.999784	1.000216	0.999655	1.000345
12	0.999678	1.000322	0.999549	1.000451
13	0.999559	1.000441	0.999430	1.000570
14	0.999429	1.000572	0.999299	1.000701
15	0.999289	1.000712	0.999160	1.000841
16	0.999131	1.000870	0.999002	1.000999
17	0.998970	1.001031	0.998841	1.001160
18	0.998782	1.001219	0.998654	1.001348
19	0.998588	1.001413	0.998460	1.001542
20	0.998388	1.001615	0.998259	1.001744
21	0.998176	1.001828	0.998047	1.001957
22	0.997956	1.002048	0.997828	1.002177
23	0.997730	1.002276	0.997601	1.002405
24	0.997495	1.002511	0.997367	1.002641
25	0.997249	1.002759	0.997120	1.002888
26	0.996994	1.003014	0.996866	1.003144
27	0.996732	1.003278	0.996603	1.003408
28	0.996460	1.003553	0.996331	1.003682
29	0.996179	1.003835	0.996051	1.003965
30	0.99589	1.00412	0.99577	1.00425
31	0.99560	1.00442	0.99547	1.00455
32	0.99530	1.00473	0.99517	1.00486
33	0.99498	1.00505	0.99485	1.00518
34	0.99465	1.00538	0.99452	1.00551
35	0.99431	1.00572	0.99418	1.00586
36	0.99396	1.00603	0.99383	1.00621
37	0.99360	1.00645	0.99347	1.00657
38	0.99323	1.00682	0.99310	1.00694
39	0.99286	1.00719	0.99273	1.00732
40	0.99248	1.00757	0.99235	1.00770
41	0.99210	1.00796	0.99197	1.00809
42	0.99171	1.00836	0.99158	1.00849

DENSITY OF WATER—(Continued).

Tempera- ture.	Density (Density at 0°=1).	Volume (Volume at 0°=1).	Density (Density at 4°=1).	Volume (Volume at 4°=1).
43	0.99131	1.00876	0.99118	1.00889
44	0.99091	1.00917	0.99078	1.00929
45	0.99050	1.00958	0.99037	1.00971
46	0.99009	1.01001	0.98996	1.01014
47	0.98967	1.01044	0.98954	1.01057
48	0.98923	1.01088	0.98910	1.01101
49	0.98878	1.01134	0.98865	1.01148
50	0.98832	1.01182	0.98819	1.01195
51	0.98785	1.01230	0.98772	1.01243
52	0.98737	1.01279	0.98725	1.01292
53	0.98689	1.01328	0.98677	1.01341
54	0.98642	1.01377	0.98629	1.01390
55	0.98594	1.01426	0.98581	1.01439
56	0.98547	1.01475	0.98534	1.01488
57	0.98499	1.01524	0.98486	1.01537
58	0.98450	1.01574	0.98437	1.01587
59	0.98401	1.01625	0.98388	1.01638
60	0.98350	1.01678	0.98338	1.01691
61	0.98299	1.01731	0.98286	1.01744
62	0.98247	1.01785	0.98234	1.01798
63	0.98194	1.01839	0.98182	1.01852
64	0.98140	1.01895	0.98128	1.01908
65	0.98086	1.01951	0.98074	1.01964
66	0.98032	1.02008	0.98019	1.02021
67	0.97977	1.02065	0.97964	1.02078
68	0.97921	1.02124	0.97908	1.02137
69	0.97864	1.02183	0.97851	1.02196
70	0.97807	1.02243	0.97794	1.02256
71	0.97749	1.02303	0.97736	1.02316
72	0.97690	1.02365	0.97677	1.02378
73	0.97631	1.02427	0.97618	1.02440
74	0.97571	1.02490	0.97558	1.02503
75	0.97511	1.02553	0.97498	1.02566
76	0.97450	1.02617	0.97438	1.02630
77	0.97389	1.02681	0.97377	1.02694
78	0.97328	1.02745	0.97316	1.02758
79	0.97267	1.02809	0.97255	1.02822
80	0.97206	1.02874	0.97194	1.02887
81	0.97145	1.02939	0.97132	1.02952
82	0.97083	1.03005	0.97070	1.03018
83	0.97020	1.03072	0.97007	1.03085
84	0.96956	1.03139	0.96943	1.03153
85	0.96892	1.03207	0.96879	1.03221
86	0.96828	1.03276	0.96815	1.03289
87	0.96764	1.03345	0.96751	1.03358
88	0.96699	1.03414	0.96687	1.03427
89	0.96634	1.03484	0.96622	1.03497
90	0.96568	1.03554	0.96556	1.03567
91	0.96502	1.03625	0.96490	1.03638
92	0.96435	1.03697	0.96423	1.03710
93	0.96368	1.03770	0.96356	1.03782

DENSITY OF WATER—(Continued).

Tempera- ture.	Density (Density at 0° = 1).	Volume (Volume at 0° = 1).	Density (Density at 4° = 1).	Volume (Volume at 4° = 1)
94	0.96300	1.03844	0.96288	1.03856
95	0.96231	1.03918	0.96219	1.03931
96	0.96161	1.03993	0.96149	1.04006
97	0.96091	1.04069	0.96079	1.04082
98	0.96020	1.04145	0.96008	1.04158
99	0.95949	1.04222	0.95937	1.04235
100	0.95879	1.04299	0.95866	1.04312

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